THE FORMATION OF A COMPLEX ION IN THE AQUEOUS SOLUTION OF SILVER NITRATE AND PHENOL.

By **Kwantaro ENDO.**

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In the study[1] of the salting out effects of neutral salts on the aqueous phenol solution, the silver nitrate has been found to be an exception in that it showed the opposite effect. It is natural to think this "salting in" effect as due to some chemical combinations between phenol and silver nitrate in the aqueous solution. The following studies were made to solve this problem.

I. The Effect of Silver Nitrate on the Partition of Phenol between Benzene and Water. The experiments on the partition of phenol between benzene and the aqueous solution of silver nitrate were carried out at 25°C. in the same manner as described in the previous paper.[2] The results are shown in Table 1, where B and C represent the molar concentrations of phenol in the benzene and in the aqueous layer respectively and S denotes that of silver nitrate.

TABLE 1.

Partition of phenol between benzene and water in the presence of $AgNO_3$.

Mol. conc. of $AgNO_3$ S	2.0		1.0		0.5		0.25	
Molar concentration of phenol in	benzene layer B	aqueous layer C	benzene layer B	aqueous layer C	benzene layer B	aqueous layer C	benzene layer B	aqueous layer C
	0.8213	0.8517	1.1136	0.5966	0.9177	0.3637	0.9561	0.3092
	0.5688	0.6965	0.7675	0.5139	0.6716	0.3139	0.6429	0.2303
	0.3647	0.5049	0.5665	0.4190	0.3905	0.2181	0.4189	0.1866
	0.2836	0.4129	0.3862	0.3197	0.1982	0.1303	0.2111	0.1174
	0.1229	0.2056	0.1697	0.1588	0.0963	0.0680	0.1079	0.0564
	0.0615	0.0988	0.0813	0.0829				

Plotting B-C curves, we obtain Fig. 1, where the observed points are denoted by circlets. In Fig. 1, the most left-sided curve, which represents the case without silver nitrate, is taken from the previous paper.[2] As we see in the figure, the curve moves to the right as the concentration of silver

(1) K. Endo, *J. Chem. Soc. Japan*, **47** (1926), 374; This Journal, **2** (1927), 124.
(2) K. Endo, This Journal, **1** (1926), 25.

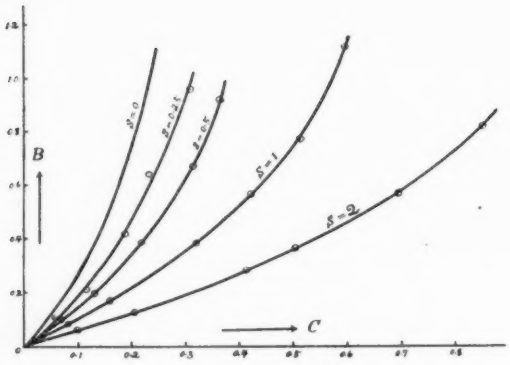

Fig. 1.

nitrate increases, that is, the solubility of phenol in the aqueous layer increases by the addition of silver nitrate. Obviously this effect is in the sense opposite to those of many other normal salts, namely, opposite to "salting out." The reason for this may be easily understood if we assume that some chemical combinations between phenol and silver nitrate (such as, the formation of a complex ion) occur in the aqueous layer. To solve this problem, I have studied, in the next place, the depression of freezing point of the aqueous solution of these substances.

II. The Effect of Silver Nitrate on the Depression of Freezing Point of the Aqueous Phenol Solution. The experiments were carried out in the similar manner as described in the previous paper. The results are shown in the following tables, where D_{P+A}, D_P and D_A represent the depressions of freezing point of the aqueous solutions of phenol in addition to silver nitrate, of phenol alone, and of silver nitrate alone, respectively.

TABLE 2.

Depression of freezing point of the aq. solution of $AgNO_3$.

Water gr.	$AgNO_3$ gr.	Molar conc. of $AgNO_3$ S	Depression (in degree) D_A
499.4	2.1370	0.0252	0.088
499.4	5.2475	0.0619	0.215
499.3	8.1625	0.0962	0.325
499.3	13.0165	0.1535	0.506
499.3	20.2700	0.2384	0.751

The data in Table 2 are also shown graphically by the curve $C=0$ in Fig. 2.

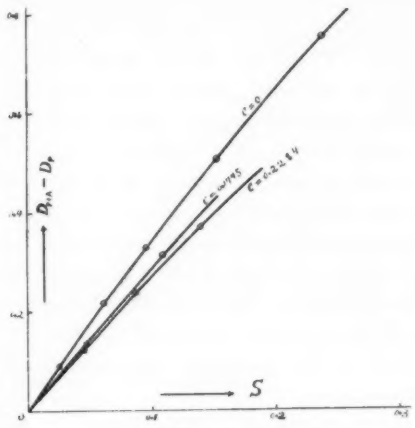

Fig. 2.

TABLE 3.

Depression of freezing point when both phenol and silver nitrate are dissolved simultaneously in water.

Water gr.	$AgNO_3$ gr.	Phenol gr.	D_{P+A} (in degree)
499.5	5.8815	2.4515	0.327
499.4	8.0345	5.7585	0.513
499.3	3.9570	8.4313	0.461
499.3	9.2870	8.4313	0.638
499.4	3.8176	10.7330	0.530
499.4	7.3333	10.7330	0.645
499.4	11.8433	10.7330	0.777

The data of Table 3 are compared in Table 4 with the summe of the individual depressions by phenol and by silver nitrate, which are obtained graphically, the former from Fig. 3 in the previous paper[1] and the latter from Fig. 2 in the present paper.

TABLE 4.

C	S	D_{P+A}	D_P	D_A	D_P+D_A
0.0522	0.0693	0.327	0.101	0.240	0.341
0.1226	0.0947	0.513	0.228	0.321	0.549
0.1795	0.0467	0.461	0.325	0.161	0.486
0.1795	0.1095	0.638	0.325	0.368	0.693
0.2284	0.0450	0.530	0.407	0.155	0.562
0.2284	0.0864	0.645	0.407	0.295	0.702
0.2284	0.1396	0.777	0.407	0.463	0.870

(1) K. Endo. This Journal, 1 (1926), 28.

Here does not hold the additivity. This is shown more clearly in Fig. 2, where the ordinate denotes $D_{P+A}-D_P$ and the abscissa the molar concentration of silver nitrate. These deviations, as in the case of partition, are in the direction opposite to those of normal cases (e. g. sodium nitrate[1]) and are moreover far greater than the latter. Such a decrease of depression must be considered as being due to the decrease of the number of dissolved particles by some chemical combinations, while all the ionised particles, on the other hand elevate[2] the activity of phenol.

III. Determination of the Chemical Equation. The aqueous solution of silver nitrate and phenol is neutral and colourless, and as no compound between these substances can be separated out in any solid state, we can not determine its formula by chemical analysis. So we are obliged to rely upon the cryoscopic method for this purpose. The observations were made in the following two extreme cases.

a) *When the concentration of silver nitrate is very small compared with that of phenol*:—In this case we may assume that the whole of silver nitrate combines with phenol. As phenol associates in triple molecules[3] in a small degree, there holds the following relation in the non-combined portion of phenol,

$$c_3 = Kc_1^3,$$

where c_1 and c_3 represent the molar concentrations of monomolecular and trimolecular phenol respectively and K the association constant. Although the initial concentration of phenol (C) is great compared to that of silver nitrate (x), its absolute value is not great. And moreover the value of K is small, so we can put

$$c_3 = KC^3$$

without introducing any serious error, because here we need only the approximate estimation and not the exact evaluation for our purpose. Thus the following depressions of freezing point are expected corresponding to the respective assumed equations.

(1) Let the aquation be

$$AgNO_3 + C_6H_5OH = [Ag.C_6H_6O]^{\cdot} + NO_3',$$

then the depression of freezing point is to be expressed by

$$D_{P+A}/k = c_1 + c_3 + C_{[Ag.C_6H_6O]^{\cdot}} + C_{NO_3'},$$

where $C_{[Ag.C_6H_6O]^{\cdot}}$ and $C_{NO_3'}$ denote the ionic concentrations of $[Ag.C_6H_6O]^{\cdot}$

(1) See the first foot-note of this paper.
(2) Ditto.
(3) K. Endo, This Journal, 1 (1926), 25.

and NO_3' respectively, and $k=1.86$. Here small correction terms due to the change of activities[1] by the presence of ions are also neglected.

Now $C = c_1+3c_3+C_{[Ag.C_6H_6O]^+}$, and $C_{[Ag.C_6H_6O]^+}=C_{NO_3'}=x$.

So $$D_{P+A}/k = C-2c_3+x = C(1-2KC^2)+x.$$

Hence $$\left(\frac{\partial D_{P+A}}{\partial x}\right)_{x=0} = k.$$

Therefore, the $D_{P+A}-x$ curve must have a tangent k at $x=0$.

(2) $$AgNO_3+C_6H_5OH = C_6H_5OAg+H^+ + NO_3',$$

then, by the treatment similar to (1), we obtain the following results,

$$D_{P+A}/k = C(1-2KC^2)+2x$$

and $$\left(\frac{\partial D_{P+A}}{\partial x}\right)_{x=0} = 2k.$$

If C_6H_5OAg dissociates further in two ions,

$$\left(\frac{\partial D_{P+A}}{\partial x}\right)_{x=0} = 3k.$$

(3) $$AgNO_3+2C_6H_5OH = [Ag.(C_6H_6O)_2]^+ + NO_3',$$

then $$D_{P+A}/k = C(1-2KC^2), \quad \text{and} \quad \left(\frac{\partial D_{P+A}}{\partial x}\right)_{x=0} = 0.$$

(4) $$AgNO_3+3C_6H_5OH = [Ag.(C_6H_6O)_3]^+ + NO_3',$$

then $$\left(\frac{\partial D_{P+A}}{\partial x}\right)_{x=0} = -k.$$

And so forth.

Now these are tested by observations, the results of which are shown in Table 5.

TABLE 5.

Depression of freez. pt. when the conc. of $AgNO_3$ is very small compared with that of phenol.

Water gr.	Phenol gr.	$AgNO_3$ gr.	x Molar conc. of $AgNO_3$	$D_{P+A}-D_P$ in degree
455.3	27.29	0.679	0.0088	0.017
455.3	27.29	1.352	0.0175	0.033
455.3	27.29	2.172	0.0281	0.051

(1) loc. cit.; Debye & Hückel, *Phys. Z.* **24** (1924), 185.

From Table 5 we obtain Fig. 3 by plotting $D_{P+A}-D_P$ against x, which becomes, as we see, a straight line represented by an equation

$$D_{P+A}-D_P = kx.$$

Its tangent is therefore

$$\left(\frac{\partial D_{P+A}}{\partial x}\right) = k.$$

which agrees whith the case of (1).

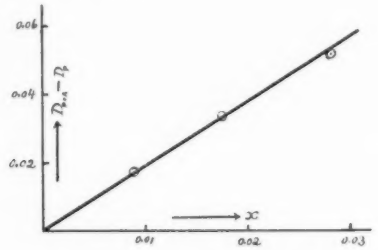

Fig. 3.

b) When the concentration of phenol is very small compared with that of silver nitrate:—The chemical equation,

$$AgNO_3 + C_6H_5OH = [Ag.C_6H_6O]^{\cdot} + NO_3^{\prime}$$

which has been proved in the last case, is tested also in this case, where we can assume that the whole of phenol combines with silver nitrate.

According to the conductivity experiments of Werner,[1] the complex salts are to be considered strong electrolytes, while according to Debye and Hückel,[2] all strong electrolytes make the perfect dissociation in the aqueous solution and the activity coefficient f_i (for the i-th ion) due to the electric field of ions is given by

$$f = e^{-Az^2\sqrt{\Sigma z_i^2 C_i}},$$

where z_i and C_i denote, respectively, the valency and the concentration of the i-th ion and A is a constant for a constant temperature. Thus,

$$D_{P+A} = k(f_1 C_{Ag^{\cdot}} + f_2 C_{NO_3^{\prime}} + f_3 C_{[Ag.C_6H_6O]^{\cdot}}).$$

As to the valencies of these ions,

$$z_1 = z_2 = z_3 = 1$$

and moreover there is the relation with regard to the analytical concentration (S) of silver nitrate,

$$\Sigma C_i = C_{Ag^{\cdot}} + C_{NO_3^{\prime}} + C_{[Ag.C_6H_6O]^{\cdot}} = 2S.$$

(1) Werner, „Neuere Anschauungen auf dem Gebiete der anorganischen Chemie."
(2) loc. cit.

So, $f_1 = f_2 = f_3 = e^{-A\sqrt{2S}} = f.$

Hence, $D_{P+A}/k = f(C_{Ag^+} + C_{NO_3^-} + C_{[Ag.C_6H_6O]^+}) = 2fS.$

Consequently, $\left(\frac{\partial D}{\partial x}\right)_{x=0} = 0$

where x represents the molar concentration of the added phenol. The experimental results are shown in Table 6 and are depicted in Fig. 4, where a straight line, given by

$$D_{P+A} - D_A = kx,$$

is also drawn for the sake of comparison.

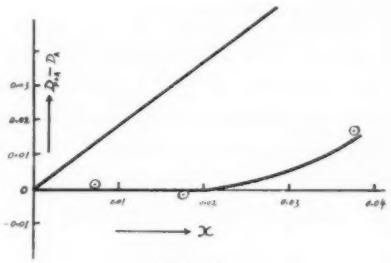

Fig. 4.

TABLE 6.

Depression of freez. pt. when the conc. of phenol is very small compared with that of silver nitrate.

AgNO gr.	Water gr.	Phenol gr.	x	$D_{P+A} - D_A$
5	35.602	0.0245	0.0073	0.001
5	35.602	0.0585	0.0175	0.002
5	35.602	0.1257	0.0375	0.017

In the vicinity of the origin, Fig. 5 shows actually a horizontal line in good agreement with our theory,

$$\left(\frac{\partial D_{P+A}}{\partial x}\right)_{x=0} = 0.$$

Thus the above chemical equation has been confirmed in the both extreme cases.

IV. Calculation of the Equilibrium Constant. As we have proved in the extreme cases that the chemical reaction,

$$AgNO_3 + C_6H_5OH = [Ag.C_6H_6O]^+ + NO_3^-$$

occurs in the aqueous solution, we shall next calculate the equilibrium constant in the intermediate cases (Table 3).

The association of phenol and the increase of activity of phenol due to the added salt are all negrected in the following calculations and the theory of strong electrolytes for dilute solutions by Debye and Hückel is applied,

for here we treat dilute solutions in the cryoscopic measurements. For the calculation of the equilibrium constant, the following ionic equation has been used,

$$C_6H_5OH + Ag^{\cdot} = [Ag.C_6H_6O]^{\cdot}.$$

As to the analytical concentrations of silver nitrate (S) and phenol (C), the following relations hold,

$$S = C_{NO_3'} = C_{Ag^{\cdot}} + C_{[Ag.C_6H_6O]^{\cdot}},$$

$$C = C_P + C_{Ag.C_6H_6O]^{\cdot}},$$

where C_P denotes the non-combined portion of phenol. For the depressions of freezing point by S moles of silver nitrate (D_A) and by C moles of phenol plus S moles of silver nitrate (D_{P+A}), respectively,

$$D_A = k(f_1 C'_A \cdot + f_2 C_{NO_3'}) = 2kfS,$$

$$D_{P+A} = k(f_1 C_A \cdot + f_2 C_{NO_3'} + f_3 C_{[Ag.C_6H_6O]^{\cdot}} + C_P) = 2kfS + kC_P.$$

Then $(D_{P+A} - D_A)/k = C_P$[1]

$$C - C_P = C_{[Ag.C_6H_6O]^{\cdot}}$$

$$S - C_{[Ag.C_6H_6O]^{\cdot}} = C_{Ag^{\cdot}}.$$

By these three equations, we can obtain the equilibrium constant K_o at 0°C as follows,

$$K_o = \frac{C_P f C_{Ag^{\cdot}}}{f C_{[Ag.C_6H_6O]^{\cdot}}} = \frac{C_P C_{Ag^{\cdot}}}{C_{[Ag.C_6H_6O]^{\cdot}}}.$$

Table 7 has been calculated from the data given in Table 4.

TABLE 7.

Calculation of the equilibrium constant.

S	C	D_{P+A}	D_A	C_P	$C_{[Ag.C_6H_6O]^{\cdot}}$	$C_{Ag^{\cdot}}$	K_o
0.0693	0.0522	0.327	0.240	0.0445	0.0077	0.0616	0.36
0.0947	0.1226	0.513	0.321	0.1010	0.0216	0.0731	0.33
0.0467	0.1795	0.461	0.161	0.1646	0.0149	0.0318	0.35
0.1095	0.1795	0.638	0.368	0.1470	0.0325	0.0770	0.35
0.0450	0.2284	0.530	0.155	0.2095	0.0189	0.0261	0.29
0.0864	0.2284	0.645	0.295	0.1943	0.0341	0.0523	0.30
0.1396	0.2284	0.777	0.463	0.1730	0.0554	0.0342	0.26
						Mean K_o = 0.32	

In spite of several neglections, the constancy of K_o is satisfactory.

(1) In the actual calculation C_P was determined graphically from the experimental D_P-C_P curve. (loc. cit.)

Summary.

1. From the measurement of partition of phenol between benzene and the aqueous solution of silver nitrate, it was found that the silver nitrate elevates considerably the solubility of phenol in the aqueous solution contrary to the salting out effects of other ordinary salts.

2. From the measurements of the depression of freezing point of the aqueous solutions of these substances, it has been proved that the "salting in" action of silver nitrate is due to the formation of a complex ion, $[Ag.C_6H_6O]^{\cdot}$, in the aqueous solution and the chemical equilibrium,

$$\dot{Ag} + C_6H_5OH = [Ag.C_6H_6O]^{\cdot},$$

is established there.

The author's thanks are due to Prof. K. Ikeda for his kind guidance in the present investigation.

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THE EFFECT OF CAUSTIC ALKALI ON THE OXIDATION OF STANNOUS CHLORIDE WITH AIR.

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S. W. Young[1] studied the effect of many substances on the oxidation of stannous chloride solution with free oxygen, but he did not studied the effect of alkali. The present research was carried out to know the effect of alkali by a modified method in connection with the former study on the effect of alkali on the oxidation of sodium sulphite with air.[2]

Experimental. The experimental procedure was quite the same with that described in the previous paper. Air was passed at constant velocity into the mixture of stannous chloride and sodium hydroxide solution. The total volume of the mixture was made to 40 c.c. in each case. A part o sodium hydroxide is used for the precipitation of stannous hydroxide, and the excess of alkali was given as C_{NaOH} in the following tables. After t-minutes the air current was stopped and the total amount of the mixture, acidified with hydrochloric acid, was poured into a known quantity of

(1) *J. Am. Chem. Soc.*, **23** (1901), 119 and 450.
(2) Miyamoto, This Journal, **2** (1927), 74.

iodine solution and the excess of iodine was titrated back with sodium thiosulphate solution. In the following tables, v is the volume of sodium thiosulphate solution of 0.0996 normal, equivalent to the amount of stannous chloride; k was calculated by $k=\frac{1}{t}(v_0-v)$, v_0 being the value of v at $t=0$, and $v_{calc.}$ was obtained by $v_{calc.}=v_0-kt$, using the mean value of k.

Table 1 shows that the oxidation velocity is independent of the amount of stannous hydroxide. When the concentration of alkali is less than about

TABLE 1.

Temp.=20°C. Velocity of air=7.78 litres per hour.

C_{NaOH} Normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.0217	0	12.08	—	—
	20	10.90	11.02	0.0590
	25	10.69	10.75	0.0556
	30	10.52	10.49	0.0520
	35	10.20	10.22	0.0537
	0	8.37	—	—
	20	7.37	7.31	0.0500
	30	6.85	6.78	0.0507
	0	5.61	—	—
	20	4.55	4.55	0.0530
	30	4.09	4.02	0.0507
			Mean:	0.0531
0.1081	0	11.94	—	—
	9	9.82	9.87	0.236
	12	9.19	9.18	0.229
	15	8.59	8.49	0.223
	20	7.40	7.34	0.227
	30	4.98	5.04	0.232
	0	6.23	—	—
	12	3.45	3.47	0.232
	17	2.33	2.33	0.229
			Mean:	0.230
0.5500	0	11.43	—	—
	10	9.13	9.28	0.230
	12	8.86	8.85	0.214
	15	8.29	8.20	0.209
	20	7.40	7.13	0.202
	30	4.61	4.98	0.227
	0	23.14	—	—
	20	18.42	18.84	0.236
	30	17.00	16.69	0.205
	0	7.57	—	—
	10	5.48	5.42	0.209
	15	4.46	4.34	0.217
			Mean:	0.215

0.2 normal in the given condition, the mixture contains white precipitates of stannous hydroxide, and the phenomenon can be explained by considering that the oxidation takes place only in the liquid phase. But in more

concentrated alkaline solutions all the precipitates dissolve, forming stannites, and it should be explained as in the case of sodium sulphite.[1]

The Effect of Sodium Hydroxide. The measurements were carried out in alkaline solutions of various concentrations, and the results are given in Table 2 and Fig. 1. The oxidation velocity of stannous hydroxide with air

TABLE 2.

Temp. = 20°C. Velocity of air = 7.78 litres per hour.

C_{NaOH} Normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.00595	0	11.39	—	—
	40	10.47	10.49	0.0230
	50	10.26	10.27	0.0226
	60	10.06	10.05	0.0222
	70	9.87	9.82	0.0217
			Mean:	0.0224
0.0217	See Table 1.			0.0531
0.04057	0	12.22	—	—
	20	10.32	10.43	0.0950
	25	10.13	9.99	0.0836
	30	9.53	9.54	0.0897
	35	9.11	9.09	0.0889
			Mean:	0.0893
0.1081	See Table 1.			0.230
0.1706	0	11.95	—	—
	10	9.19	9.38	0.276
	15	8.17	8.09	0.252
	20	6.88	6.81	0.254
	25	5.50	5.52	0.258
	30	4.57	4.24	0.246
			Mean:	0.257
0.2204	0	12.32	—	—
	9	9.88	9.99	0.271
	12	9.20	9.21	0.260
	14	8.85	8.69	0.256
	20	7.24	7.14	0.254
	24	6.24	6.10	0.253
			Mean:	0.259
0.3252	0	12.18	—	—
	9	9.80	9.97	0.264
	12	9.20	9.23	0.248
	15	8.54	8.49	0.243
	20	7.40	7.26	0.239
	25	6.33	6.03	0.234
			Mean:	0.246
0.5500	See Table 1.			0.215
1.130	0	12.65	—	—
	10	10.90	10.97	0.175
	12	10.68	10.63	0.164
	15	10.10	10.13	0.170
	20	9.29	9.29	0.168
	30	7.77	7.61	0.163
			Mean:	0.168
1.704	0	12.02	—	—
	20	9.32	9.50	0.135
	25	8.87	8.87	0.126
	30	8.36	8.24	0.122
	36	7.69	7.48	0.120
			Mean:	0.126
2.312	0	7.53	—	—
	10	6.49	6.53	0.104
	12	6.37	6.33	0.0967
	15	5.92	6.03	0.107
	20	5.63	5.53	0.0950
	27	4.93	4.84	0.0963
			Mean:	0.0998

(1) Previous paper.

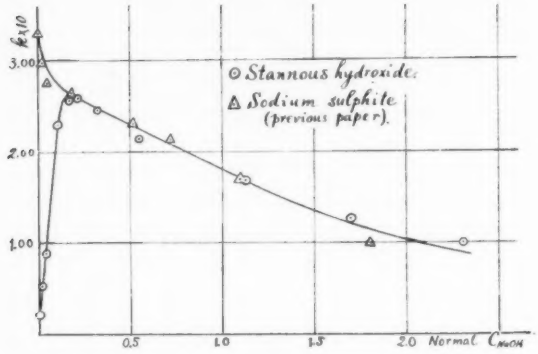

Fig. 1.

increases rapidly with the increase of the concentration of alkali until it attains a certain value and then decreases slowly. It was observed that the mixture contains white precipitates until the oxidation velocity attains almost its maximum value. In more concentrated alkaline solutions, all the stannous hydroxide dissolves forming stannites and the oxidation velocity was found to be the same as that of sodium sulphite. The results can be explained as follows.

The oxidation velocity increases until it attains the dissolution velocity of air with the increase of the concentration of alkali, which causes the formation of stannites. When the concentration of alkali increases still more, the dissolution velocity of air decreases, and consequently the oxidation velocity decreases. This assumption, which was also employed for the explanation of the oxidation velocity of sodium sulphite, was ascertained by the coincidence of their velocity constants as shown in Fig. 1. The values thus obtained can be regarded as the dissolution velocity of oxygen, when air was passed into 40 c.c. of solution in a test tube (diameter 3 cm.) through a glass tube (inside diameter = 4 mm. outside diameter = 6 mm.) at the rate of 7.78 litres per hour. From Fig. 1 we can calculate the approximate values of dissolution velocity of oxygen under the condition above described. Thus,

C_{NaOH} Normal	k	Dissolution velocity of oxygen
0.50	0.230	5.7×10^{-6} mols per minute.
1.00	0.180	4.5×10^{-6}
1.50	0.136	3.4×10^{-6}

The Effect of Temperature. The oxidation velocities at 30°C. and 40°C. are given in Table 3. The effect of temperature was small.

TABLE 3.

Velocity of air=7.78 litres per hour.

Temp.	C_{NaOH} Normal	min.	v c.c.	$v_{calc.}$ c.c.	k
30°C.	0.0217	0	11.57	—	—
		30	8.99	9.16	0.0860
		35	8.76	8.76	0.0803
		40	8.56	8.56	0.0753
		50	7.61	7.56	0.0792
				Mean:	0.0802
30°C.	0.5500	0	11.14	—	—
		12	8.22	8.26	0.243
		15	7.44	7.54	0.247
		20	6.40	6.34	0.237
		25	5.32	5.14	0.233
				Mean:	0.240
40°	0.0217	0	10.35	—	—
		15	8.82	8.88	0.1020
		20	8.41	8.39	0.0970
		25	7.86	7.90	0.0996
		40	6.65	6.44	0.0925
				Mean:	0.0978
40°C.	0.5500	0	12.02	—	—
		10	9.17	9.22	0.285
		15	7.81	7.82	0.281
		20	6.50	6.42	0.276
		25	5.07	5.02	0.278
				Mean:	0.280

$\frac{k_{30°}}{k_{20°}}=\frac{0.0802}{0.0531}=1.51$ $\frac{k_{40°}}{k_{30°}}=\frac{0.0978}{0.0802}=1.22$ When $C_{NaOH}=0.0217$ normal

$\frac{k_{30°}}{k_{20°}}=\frac{0.240}{0.215}=1.12$ $\frac{k_{40°}}{k_{30°}}=\frac{0.280}{0.240}=1.17$ When $C_{NaOH}=0.5500$ normal

The Effect of the Velocity of Air Passed. It will be seen from Table 4 that a small change of the velocity of air current has not much influence on the oxidation velocity.

TABLE 4.

Temp.=20°C. C_{NaOH}=0.5500 Normal.

Velocity of air litres/hour	t min.	v c.c.	$v_{calc.}$ c.c.	k
6.67	0	11.31	—	—
	15	8.13	8.26	0.212
	20	7.11	7.25	0.210
	25	6.43	6.23	0.195
	30	5.35	5.22	0.199
			Mean:	0.203
10.00	0	11.81	—	—
	9	9.65	9.70	0.240
	15	8.35	8.30	0.231
	20	7.19	7.13	0.231
	25	5.96	5.96	0.234
			Mean:	0.234

Summary.

(1) The oxidation velocity of stannous chloride in alkaline solutions with air was studied. It was found to be the same as that of sodium sulphite when the concentration of alkali is greater than about 0.2 normal under the given condition.

(2) The effect of temperature was small.

(3) The dissolution velocity of oxygen in alkaline solutions was calculated indirectly.

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THE VISCOSITY OF LIQUIDS ABOVE THEIR BOILING POINTS. PART II.[1]

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Relation between Viscosity and Volume or Temperature.

1. Definition of Molecular and Specific Fluidity. The coefficient of viscosity η is defined by the formula:

$$R = \eta \cdot \frac{dv}{dz} \cdot A.$$

where R is tangential resistance, $\frac{dv}{dz}$ velocity gradient along the normal and A area. Therefore, it may also be defined as follows: we consider at first an unit cube (Fig. 1.) filled with a viscous substance. The viscosity of the substance is measured by the tangential resistance R on the upper plane of the cube, when it moves with unit velocity in respect to the lower.

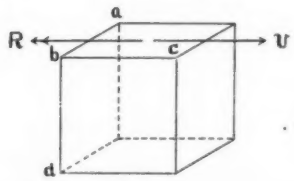


Fig. 1.

In order to express the viscosity in a molecular term, Thorpe and Rodger[2] proposed the molecular viscosity, which is defined by the product $\eta \cdot V^{\frac{2}{3}}$, V being molecular volume, so that the molecular viscosity after Thorpe and Rodger is equal to the resistance when the sliding surface contains equal number of molecules, i.e. when in Fig. 1. $ab = bc = V^{\frac{1}{3}}$ while $bd = 1$. The conception of this quantity seems not to be adequate, since, although equal number of molecules are arranged for different substances along ab and bc, it is not so in the direction bd. The expression $\eta \cdot V^{\frac{2}{3}}$ may strictly be called molecular surface viscosity. The true molecular viscosity should be defined as follows: the molecular viscosity is measured by the resistance when the same number of molecules are arranged also in the direction of normal bd, i.e. when $ab = bc = bd = V^{\frac{1}{3}}$ in Fig. 1. Putting $ab = bc = bd = V_1^{\frac{1}{3}}$ where V_1 is specific volume, specific viscosity may similarly be defined.

(1) Part I, This Journal, **2** (1927), 95.
(2) Thorpe and Rodger, *Phil. Trans.*, (A), **185** (1894), 397.

As the term of molecular viscosity are already conventionally understood in the sense of Thorpe and Rodger, the writer proposes to introduce the new proper definition for molecular and specific fluidity as the reciprocal of the above two quantities.

The coefficient of fluidity, denoted by ϕ, is the reciprocal of the coefficient of viscosity, so that it may be defined as the velocity v given to the upper plane referred to the lower (Fig. 1), by unit tangential force applied to the upper plane. Consequently, molecular fluidity Φ is measured by the sliding velocity given by unit tangential force applied to a plane containing the same number of molecules for different substances, the velocity being referred to another fixed plane, the distance between the two planes also having the same number of molecules. In Fig. 1., when $ab=bc=bd=V^{\frac{1}{3}}$, the velocity v measures molecular fluidity Φ. Specific fluidity Φ_1 is similarly defined as the velocity v in Fig. 1. when $ab=bc=bd=V_1^{\frac{1}{3}}$.

These two quantities can be calculated from the value of viscosity η or fluidity ϕ and molecular V or specific volume V_1 from the following relations:

$$\Phi = \frac{\phi}{V^{\frac{1}{3}}} = \frac{1}{\eta \cdot V^{\frac{1}{3}}} \quad \ldots\ldots(1)$$

$$\Phi_1 = \frac{\phi}{V_1^{\frac{1}{3}}} = \frac{1}{\eta \cdot V_1^{\frac{1}{3}}} \quad \ldots\ldots(2)$$

2. Relation between Molecular Fluidity and Molecular Volume. As the relation between viscosity η and specific volume V_1, Batschinski[1] put forward the following experimental formula:

$$\eta = \frac{c}{(V_1 - \omega)} \quad \ldots\ldots(3)$$

where c and ω are constants. This relation seems to have little theoretical lucidity, since viscosity in the left side is referred to unit cube, while specific volume in the right side being referred to one gram.

We will consider the molecular fluidity defined above as regards its relation to the molecular volume. Suppose the upper plane of the cube in Fig. 1 is displaced in reference to the lower by the amount du during the time $d\theta$ by unit tangential force applied to the upper plane. Then the displacement du measures the amount of shear of the vertical side. Therefore it seems plausible to assume this displacement to be proportional to the free space in the plane cbd, i.e. the area of the plane decreased by the amount proportional to the section of molecules:

(1) Batschinski, *Z. physik. Chem.*, **84** (1913), 643.

$$du = K.(V^{\frac{2}{3}} - B^{\frac{2}{3}}).d\theta.$$

where K and B are constants. Dividing both sides with $d\theta$ and taking into consideration that $\frac{du}{d\theta}$ is equal to molecular fluidity Φ, the above relation becomes,

$$\Phi = K.(V^{\frac{2}{3}} - B^{\frac{2}{3}}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

The constant B is the limiting value of the molecular volume of liquid as its molecular fluidity approaches zero, and it is therefore called effective molecular volume. Calling the difference $(V^{\frac{2}{3}} - B^{\frac{2}{3}})$ the molecular free area, the above relation may be expressed as follows: the molecular fluidity varies directly as the molecular free area.

Similarly, for the specific fluidity we obtain the following relation:

$$\Phi_1 = K_1.(V_1^{\frac{2}{3}} - B_1^{\frac{2}{3}}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

were K_1 and B_1 are constants having similar meanings as K and B and being related with them by the equations:

$$K_1 = M.K, \quad \text{and} \quad B_1 = \frac{B}{M}.$$

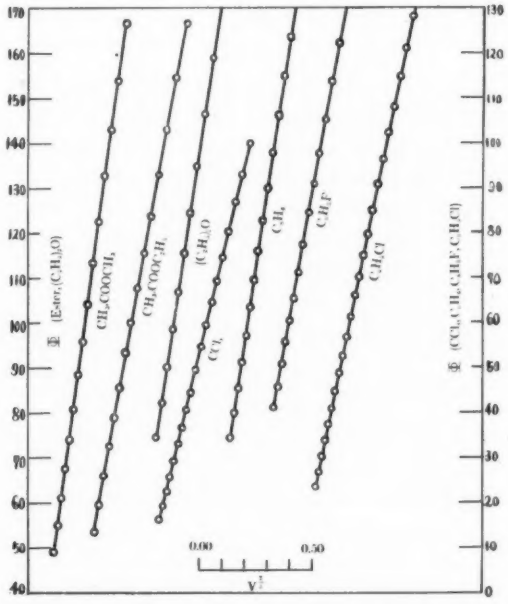


Fig. 2.—The volume relation for organic liquids extended over boiling points.

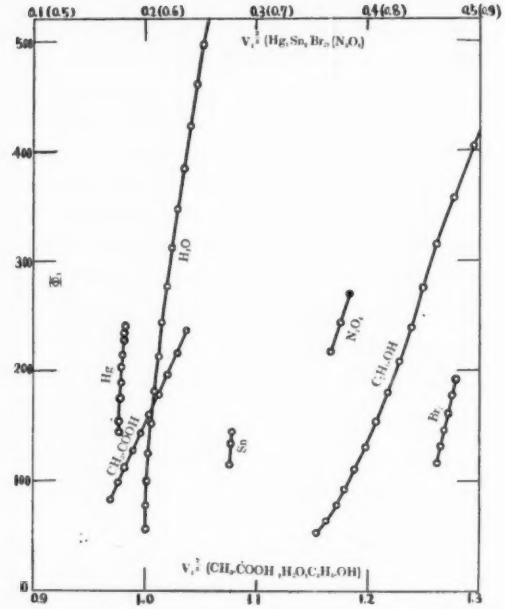


Fig. 3.—The volume relation for abnormal and inorganic liquids.

where M being the molecular weight. The above two relations (4) and (5) will be called the volume relation.[1] This is graphically summarised in Figs. 2. and 3., the details of numerical data are given in later tables. The volume relation is found to be satisfied by many substances. The calculated values of molenular or specific fluidity seldom deviate from the observed values by more than one per cent. Few substances for which the agreement is not good include alcohols, water and mercury, so long as being tested.

Multiplying both sides of the equation (5) with $V_1^{\frac{1}{3}}$ and inverting it, we have:

$$\eta = \frac{\frac{1}{K_1}}{(V_1 - B_1^{\frac{3}{3}}.V_1^{\frac{1}{3}})} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Comparing this expression with that of Batschinski (3), we see that a constant ω in the latter corresponds to a variable $B_1^{\frac{3}{3}}.V_1^{\frac{1}{3}}$ in the former (6).

(1) Although the definition of molecular or specific fluidity and their relation to volume need the data of density, this is not accompanied by introduction of a new unknown quantity, since the value of density is always necessary for the measurement of viscosity.

The effect due to this difference in formula may not be large until a comparison is done over a wide temperature range up to the critical point, but in this case a remarkable difference would appear between the values calculated by each equation.

3. Relation between Molecular Fluidity and Temperature. Viscosity or fluidity is one of the properties which change most remarkably with temperature, and as regards their variation with temperature, so many equations have been proposed that one can hardly decide which one is to be preferred.

If the volume relation obtained above be correct from the freezing point up to the critical, the molecular fluidity would approach zero at a certain low temperature, while near the critical it would increase very rapidly to a certain critical value. As one of the formula satisfying these conditions and containing constants as few as possible, the following relation is proposed:

$$\log(\Phi_K - \Phi) = \frac{1}{5}\log(T_K - T) + \text{Const.}$$

or

$$(\Phi_K - \Phi) = C.(T_K - T)^{\frac{1}{5}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

where T_K is critical temperature, Φ_K the value of molecular fluidity at this point, C a constant. Similarly, for the specific fluidity:

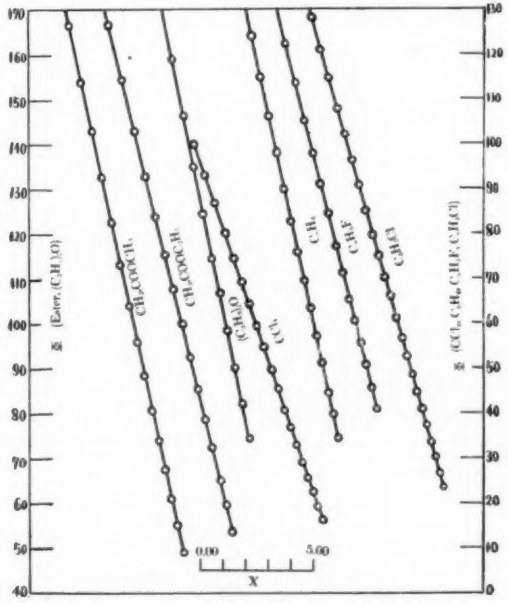


Fig. 4.—The temperature relation for organic liquids extended over boiling points.

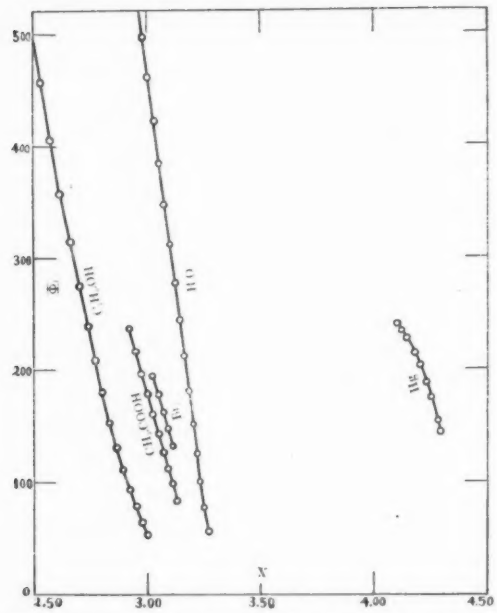


Fig. 5.—The temperature relation for abnormal and inorganic liquids.

$$(\Phi_{1K} - \Phi_1) = C_1 . (T_K - T)^{\frac{1}{5}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where respective quantities are each referred to one gram and—

$$C_1 = M^{\frac{1}{3}} . C. \qquad \Phi_{1K} = M^{\frac{1}{3}} . \Phi_K .$$

M being the molecular weight. These relations will be called temperature relation. The temperature relation was found to be satisfied by many substances with a few exceptions (alcohols, water and mercury so long as being tested) as being shown graphically in Figs. 4. and 5. and numerically in later tables.

Notation:—t: Temperature in Celcius degree.

Φ: Molecular fluidity observed.

Φ_V: Molecular fluidity calculated from volume.

Φ_T: Molecular fluidity calculated from temperature.

Constants K, C etc. were determined graphically. Most of the necessary data were taken from the papers of S. Young,[1] Thorpe and Rodger,[2]

1) Density: S. Young, *Sci. Proc. Roy. Dublin Soc.*, **12** (1909–1910), 374.

2) Viscosity: Thorpe & Rodger, *Phil. Trans.*, (A), **185** (1894), 397; ibid., **189** (1897), 71.

A. Heydweiller[1] and the writer's own.[2] A few others were from the Tables of Landolt-Börnstein-Roth, 5 edition.

Normal Pentane.

$\Phi_V = 31.8\ (V^{\frac{2}{3}} - 95.50^{\frac{2}{3}})$.

$\Phi_T = 795.4 - 251\ (197{,}2 - t)^{\frac{1}{3}}$.

t	Φ	Φ_V	Φ_T
0	73.36	73.5	73.5
10	80.87	80.7	80.7
20	88.59	88.7	88.5
30	96.47	96.4	96.7

Isopentane.

$\Phi_V = 32.1\ (V^{\frac{2}{3}} - 96.10^{\frac{2}{3}})$.

$\Phi_T = 799.5 - 254\ (187.8 - t)^{\frac{1}{3}}$.

t	Φ	Φ_V	Φ_T
0	75.82	75.8	75.9
10	83.71	83.7	83.7
20	91.85	91.7	91.9
30	99.86	100.3	99.7

Normal Hexane.

$\Phi_V = 25.4\ (V^{\frac{2}{3}} - 112.6^{\frac{2}{3}})$.

$\Phi_T = 702.6 - 219\ (234{,}8 - t)^{\frac{1}{3}}$.

t	Φ	Φ_V	Φ_T
0	50.16	50.3	50.2
10	55.77	55.9	55.7
20	61.60	61.6	61.7
30	67.63	67.7	67.7
40	73.98	73.8	74.1
50	80.63	80.5	80.7
60	87.46	87.7	87.5

Normal Heptane.

$\Phi_V = 21.7\ (V^{\frac{2}{3}} - 129.9^{\frac{2}{3}})$.

$\Phi_T = 660.1 - 204\ (266.85 - t)^{\frac{1}{3}}$.

t	Φ	Φ_V	Φ_T
0	36.84	36.8	36.5
10	41.40	41.4	41.4
20	46.20	45.9	46.2

Normal Heptane.

(continued)

30	51.21	51.5	51.3
40	56.32	56.5	56.4
50	61.81	62.2	61.9
60	67.54	67.4	67.4
70	73.37	73.3	73.3
80	79.62	79.5	79.5
90	85.90	85.3	86.3

Normal Octane.

$\Phi_V = 18.6\ (V^{\frac{2}{3}} - 147.9^{\frac{2}{3}})$.

$\Phi_T = 612.9 - 188\ (296.2 - t)^{\frac{1}{3}}$.

t	Φ	Φ_V	Φ_T
0	26.26	25.8	26.1
10	30.02	29.7	30.1
20	34.06	34.1	34.3
30	38.15	38.5	38.5
40	42.48	42.5	42.8
50	46.97	47.2	47.3
60	51.60	52.0	51.9
70	56.48	56.7	56.9
80	61.56	61.8	62.0
90	66.92	66.9	67.3
100	72.46	72.7	72.5
110	78.18	78.3	78.1
120	84.57	84.0	84.0

Methyl-formate.

$\Phi_V = 43.8\ (V^{\frac{2}{3}} - 52.04^{\frac{2}{3}})$.

$\Phi_T = 729.5 - 229\ (214.0 - t)^{\frac{1}{3}}$.

t	Φ	Φ_V	Φ_T
0	59.60	59.7	59.8
10	66.27	66.3	66.2
20	72.98	72.7	72.8
30	79.47	79.7	79.7

Ethyl-formate.

$\Phi_V = 34.0\ (V^{\frac{2}{3}} - 69.60^{\frac{2}{3}})$.

$\Phi_T = 696.1 - 218\ (235.3 - t)^{\frac{1}{3}}$.

(1) Viscosity above boiling points: A. Heydweiller, *Wied. Ann.*, **55** (1895), 561; ibid., **59** (1896), 198.

(2) Viscosity above boiling points: the writer, this paper part I. (loc. cit.)

Ethyl-formate.
(continued)

t	Φ	Φ_V	Φ_T
0	46.32	46.2	46.3
10	51.96	52.2	51.8
20	57.66	57.7	57.7
30	63.72	63.9	63.7
40	70.00	69.8	70.0
50	76.28	76.3	76.6

Propyl-formate.

$\Phi_V = 27.5\ (V^{\frac{2}{3}} - 86.82^{\frac{2}{3}})$.

$\Phi_T = 649.3 - 202\ (264.85 - t)^{\frac{1}{5}}$.

t	Φ	Φ_V	Φ_T
0	32.83	32.9	32.7
10	37.40	37.3	37.4
20	42.17	42.3	42.4
30	47.19	47.2	47.4
40	52.47	52.5	52.5
50	57.85	57.9	58.0
60	63.50	63.5	63.6
70	69.37	69.3	69.4
80	75.54	75.5	75.5

Methyl-acetate.

$\Phi_V = 37.1\ (V^{\frac{2}{3}} - 68.93^{\frac{2}{3}})$.

$\Phi_T = 742.4 - 233\ (233.7 - t)^{\frac{1}{5}}$.

t	Φ	Φ_V	Φ_T
0	49.14	48.9	48.8
10	55.00	54.8	54.8
20	61.09	61.1	61.0
30	67.35	67.4	67.6
40	73.89	74.2	74.4
50	80.78	81.3	81.4
60	88.47	88.5	88.8
70	95.81	96.0	96.4
80	104.0	104.4	104.6
90	113.3	112.5	113.0
100	122.6	121.7	122.1
110	132.7	131.7	131.6
120	142.9	142.3	141.9
130	153.8	153.9	152.9
140	166.6	166.6	164.7

Ethyl-acetate.

$\Phi_V = 28.2\ (V^{\frac{2}{3}} - 86.10^{\frac{2}{3}})$.

$\Phi_T = 674.4 - 211\ (250.1 - t)^{\frac{1}{5}}$.

Ethyl-acetate.
(continued)

t	Φ	Φ_V	Φ_T
30	53.53	54.1	53.9
40	59.73	59.7	59.5
50	66.03	65.7	65.6
60	72.41	71.7	71.7
70	78.83	78.8	78.2
80	85.59	85.0	85.1
90	92.68	92.0	92.0
100	100.1	99.1	99.5
110	107.7	107.1	107.4
120	115.5	115.5	115.8
130	123.8	124.4	124.6
140	132.9	133.4	134.0
150	143.1	144.6	144.2
160	154.5	155.9	155.4
170	166.7	168.7	167.4
180	179.9	182.3	180.7

Propyl-acetate.

$\Phi_V = 23.8\ (V^{\frac{2}{3}} - 104.2^{\frac{2}{3}})$.

$\Phi_T = 630.0 - 196\ (276.2 - t)^{\frac{1}{5}}$.

t	Φ	Φ_V	Φ_T
0	26.93	23.7	24.7
10	31.04	31.0	31.2
20	35.40	35.4	35.7
30	40.09	40.2	40.4
40	44.83	45.0	45.2
50	49.77	50.1	50.3
60	55.00	55.4	55.5
70	60.36	60.8	60.8
80	66.00	66.4	66.7
90	72.19	72.6	72.4
100	79.30	78.6	78.6

Methyl-propionate.

$\Phi_V = 28.9\ (V^{\frac{2}{3}} - 85.04^{\frac{2}{3}})$.

$\Phi_T = 669.2 - 208\ (257.4 - t)^{\frac{1}{5}}$.

t	Φ	Φ_V	Φ_T
0	37.82	37.8	37.9
10	42.80	43.0	42.9
20	48.06	47.9	48.0
30	53.26	53.0	53.3
40	58.79	58.7	58.9
50	64.46	64.7	64.6
60	70.49	70.5	70.5
70	76.85	76.5	76.8

Ethyl-propionate.

$\Phi_V = 23.5\ (V^{\frac{2}{3}} - 102.9^{\frac{2}{3}})$.

$\Phi_T = 628.5 - 195\ (272.9 - t)^{\frac{1}{5}}$.

Ethyl-propionate.
(continued)

t	Φ	Φ_V	Φ_T
0	29.94	29.8	29.8
10	34.22	34.3	34.2
20	38.69	38.6	38.9
30	43.43	43.3	43.6
40	48.30	48.4	48.6
50	53.37	53.7	53.6
60	58.60	58.9	58.8
70	64.19	64.2	64.2
80	70.01	69.9	69.9
90	76.05	76.0	75.8

Methyl-butyrate.

$\Phi_V = 23.6\ (V^{\frac{2}{3}} - 102.7^{\frac{2}{3}})$.

$\Phi_T = 623.5 - 193\ (281.3 - t)^{\frac{1}{3}}$.

t	Φ	Φ_V	Φ_T
0	27.43	27.4	27.3
10	31.55	31.9	31.5
20	35.91	36.0	36.0
30	40.48	40.6	40.6
40	45.20	45.5	45.3
50	50.08	50.4	50.2
60	55.22	55.4	55.2
70	60.50	60.5	60.4
80	66.16	65.8	65.8
90	72.01	71.4	71.5
100	77.82	77.2	77.3

Methyl-isobutyrate.

$\Phi_V = 23.8\ (V^{\frac{2}{3}} - 102.9^{\frac{2}{3}})$.

$\Phi_T = 624.0 - 194\ (267.55 - t)^{\frac{1}{3}}$.

t	Φ	Φ_V	Φ_T
0	30.84	30.6	30.7
10	35.20	35.2	35.2
20	39.72	39.8	39.8
30	44.43	44.7	44.6
40	49.38	49.8	49.6
50	54.59	54.8	54.7
60	59.89	60.1	60.0
70	65.54	65.5	65.5
80	71.48	71.5	71.4
90	77.82	77.3	77.3

Ethyl-ether.

$\Phi_V = 33.8\ (V^{\frac{2}{3}} - 85.69^{\frac{2}{3}})$.

$\Phi_T = 791.0 - 250\ (193.8 - t)^{\frac{1}{3}}$.

Ethyl-ether.
(continued)

t	Φ	Φ_V	Φ_T
0	74.40	74.3	74.2
10	82.24	82.4	81.8
20	90.16	89.9	89.7
30	98.42	98.3	97.9
40	106.8	107.3	106.6
50	115.4	116.0	115.9
60	124.6	125.1	125.4
70	135.0	135.3	135.8
80	146.6	145.9	146.9
90	159.1	158.8	158.5
100	172.6	171.8	171.2

Carbon-tetrachloride.

$\Phi_V = 20.4\ (V^{\frac{2}{3}} - 88.88^{\frac{2}{3}})$.

$\Phi_T = 470.7 - 147\ (283.15 - t)^{\frac{1}{3}}$.

t	Φ	Φ_V	Φ_T
0	16.31	16.1	16.1
10	19.32	19.5	19.3
20	22.50	22.6	22.6
30	25.75	26.4	26.1
40	29.27	29.6	29.6
50	33.08	33.6	33.3
60	36.65	37.3	37.2
70	40.74	41.4	41.1
80	45.41	45.3	45.2
90	49.65	49.7	49.5
100	54.82	54.2	53.9
110	59.50	58.6	58.6
120	64.49	63.8	63.7
130	69.29	68.8	68.5
140	74.64	74.3	73.9
150	80.33	79.9	79.7
160	87.02	85.5	85.7
170	93.22	92.1	92.2
180	100.0	98.6	99.2

Benzene.

$\Phi_V = 34.4\ (V^{\frac{2}{3}} - 82.21^{\frac{2}{3}})$.

$\Phi_T = 756.6 - 236\ (288.5 - t)^{\frac{1}{3}}$.

t	Φ	Φ_V	Φ_T
20	34.62	34.3	34.3
30	39.92	39.7	39.8
40	45.47	45.8	45.4
50	51.18	51.6	51.3
60	57.18	57.7	57.3
70	63.37	63.3	63.5
80	69.58	69.9	70.0
90	75.95	75.3	75.6
100	82.75	83.3	83.6

Benzene.

(continued)

110	90.10	90.4	91.0
120	97.95	98.0	97.6
130	106.3	106.0	106.6
140	115.1	114.9	115.0
150	124.3	124.0	123.9
160	134.1	132.9	133.3
170	144.6	143.4	143.2
180	155.4	153.7	154.0

Fluorobenzene.

$\Phi_V = 28.8\ (V^{\frac{2}{3}} - 85.51^{\frac{2}{3}})$.

$\Phi_T = 647.3 - 200\ (286.55 - t)^{\frac{1}{3}}$.

t	Φ	Φ_V	Φ_T
30	41.19	40.9	40.9
40	45.66	45.6	45.6
50	50.81	50.3	50.5
60	55.71	55.5	55.6
70	60.38	60.8	61.1
80	65.25	65.9	66.5
90	71.22	72.1	72.3
100	77.32	78.2	78.1
110	84.45	84.4	84.5
120	91.11	91.2	91.0
130	97.81	98.4	97.8
140	105.2	105.7	105.0
150	113.7	113.4	112.6
160	122.4	122.8	120.7
170	131.0	130.4	129.2
180	141.0	139.6	138.4

Chlorobenzene.

$\Phi_V = 24.5\ (V^{\frac{2}{3}} - 94.12^{\frac{2}{3}})$.

$\Phi_T = 601.1 - 179\ (359.2 - t)^{\frac{1}{3}}$.

t	Φ	Φ_V	Φ_T
10	23.70	23.6	23.6
20	26.81	27.0	27.0
30	30.29	30.5	30.4
40	33.66	34.0	34.0
50	37.42	37.5	37.5
60	41.06	41.2	41.2
70	44.74	45.0	45.1
80	48.72	48.8	48.9
90	52.70	53.0	53.0
100	56.80	56.8	57.0
110	61.27	61.2	61.3
120	65.10	65.7	65.6
130	70.31	70.5	70.3
140	74.89	75.1	75.0
150	79.74	79.8	79.9
160	85.13	84.9	84.7
170	90.84	90.2	90.2
180	96.49	95.8	95.7
190	102.3	101.6	101.5
200	107.9	107.8	107.6
210	114.8	114.4	113.9
220	121.2	120.9	120.7
230	128.3	128.5	127.7
240	135.5	136.8	135.3

For the following substances quantities are all referred to one gram and this is meant by the index 1 under the symbol.

Acetic acid.

$\Phi_{1V} = 2250\ (V_1^{\frac{2}{3}} - 0.8997^{\frac{2}{3}})$.

$\Phi_{1T} = 2291 - 705\ (321.6 - t)^{\frac{1}{3}}$.

t	Φ_1	Φ_{1V}	Φ_{1T}
20	83.32	83	82
30	97.74	96	97
40	112.0	112	113
50	127.2	127	128
60	143.1	144	144
70	159.7	160	162
80	177.6	178	178
90	196.2	196	197
100	215.7	215	215
110	235.8	234	234

Bromine.

$\Phi_{1V} = 4400\ (V_1^{\frac{2}{3}} - 0.2868^{\frac{2}{3}})$.

$\Phi_{1T} = 2273 - 688\ (302.2 - t)^{\frac{1}{3}}$.

t	Φ_1	Φ_{1V}	Φ_{1T}
0	117.0	117	117
10	132.3	132	132
20	147.1	147	147
30	162.0	161	161
40	177.5	177	178
50	193.6	194	194

Nitrogen peroxide.

$\Phi_{1V} = 3250\ (V_1^{\frac{2}{3}} - 0.5855^{\frac{2}{3}})$.

t	Φ_1	Φ_{1V}
0	216.6	217
10	242.9	243
20	270.4	270

Molten Tin.

$\Phi_{1V} = 16000\ (V_1^{\frac{2}{3}} - 0.1247^{\frac{2}{3}})$.

t	Φ_1	Φ_{1V}
280	113.8 (110.4?)	111
296	114.7	115
357	134.0	134
389	145.1	144

?: Extrapolated from the other temperatures.

From above results, it may be concluded that equations (4), (7), etc. expressing the relations among molecular fluidity ($^1/_{\eta}.V^{\frac{1}{3}}$), molecular volume and absolute temperature hold good for most substances except a few which include alcohols, water and mercury.

In conclusion, the writer wishes to express his cordial thanks to Prof. M. Katayama for his kind guidance.

April, 1927.

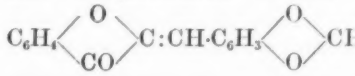
The Institute of Physical and Chemical Research,
Hongo, Tokyo.

SYNTHESE VON 3′,4′-METHYLENDIOXYFLAVON, 3′,4′-METHYLENDIOXYFLAVONOL, 3′,4′-DIMETHOXYFLAVON UND 3′,4′-DIMETHOXYFLAVONOL.

Von **Shizuo HATTORI.**

Eingegangen am 11. April 1927. Ausgegeben am 28. Juni 1927.

Zum Zweck der Verwendung zu meiner spektrographischen Untersuchung habe ich die oben genannten Flavone und Flavonole neu synthetisiert. Die Synthese der ersten Verbindung hatten W. Feuerstein und St. v. Kostanecki[1] schon früher versucht, aber es resultierte aus dem 2-Acetoxy-3′,4′-methylendioxychalkondibromid beim Behandeln mit Kalilauge kein entsprechendes Flavon, sondern das gelbe Piperonalcumaranon,



Diese Darstellungsweise[2] eines

(1) W. Feuerstein u. St. v. Kostanecki, *Ber.*, **32** (1899), 315.
(2) T. Emilewicz u. St. v. Kostanecki, *Ber.*, **31** (1898), 696.

Flavons aus o-Acetoxychalkondibromid geht sehr glatt bei 7-Oxyflavon[1] (aus 2-Acetoxy-4-äthoxychalkondibromid) und 7-Äthoxy-4-methoxyflavon[2] u.s.w., dagegen schlägt die Methode fehl bei Flavon[3] (aus 2-Acetoxychalkondibromid), 4′-Methoxyflavon[4] (aus 4′-Methoxy-2-acetoxychalkondibromid) und bei 3′,4′-Methylendioxyflavon, wobei hauptsächlich Cumaranonderivate nebst einer gelingen Menge von Flavonen entstehen.

In vorliegenden synthetischen Versuchen habe ich eine schöne von A. Löwenbein[5] aufgefundene Reaktion angewandt, welche in Dehydrierung eines Flavanons durch Einwirkung des Phosphorpentachlorids besteht. Diese Methode der Flavonsynthese ist als die beste zu empfehlen, wenn man das Flavanon schon in den Händen hat. Durch diese Methode konnte auch die Synthese des 3′,4′-Methylendioxyflavons leicht durchgeführt werden.

Die Flavonole sind auch nach der Methode von Kostanecki[6] synthetisiert; nämlich eine Umwandlung von Flavanon über Isonitrosoflavanon in Flavonol, welche Reaktion auch glatt vor sich ging.

Versuche.

3′,4′-Methylendioxyflavanon. Eine heisse Lösung von 3′,4′-Methylendioxy-2-oxychalkon[7] vom Schmp. 140° in Alkohol wird mit 10 proz. Schwefelsäure versetzt und auf dem lebhaft siedenden Wasserbade 24 Stunden lang erhitzt. Beim Erkalten scheiden sich weisse Nadeln vom Flavanon aus, die mit etwas unverändertem Chalkon beigemengt sind. Nach vollständigem Abscheiden filtriert man sie ab, spült mit Wasser zur Befreiung von Schwefelsäure aus und trocknet in einem Exsikkator. Dann wird die Krystallmasse beim gelinden Erwärmen in verhältnismässig viel Schwefelkohlenstoff gelöst und stehen gelassen, wobei das schwerer lösliche Flavanon in derben weissen Tafeln auskrystallisiert, dagegen das unveränderte Chalkon in Lösung bleibt. Dieses erstere wird aus 80 proz. Alkohol umkrystallisiert, woraus sie in glänzenden farblosen prismatischen Nadeln ausscheiden. Aus noch wasserärmerem Alkohol erhält man sie in hübschen, glitzernden, kurzen Prismen. Beide sind vom Schmp. 127–128°. ($C_{16}H_{12}O_4$. Ber.: C = 71.64, H = 4.46; Gef.: C = 71.73, H = 4.77%).

Mit conz. Schwefelsäure betupft, färben sich die Krystalle frisch ziegelrot.

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(1) T. Emilewicz u. St. v. Kostanecki, loc. cit., S. 698.
(2) St. v. Kostanecki u. F. Wosius, *Ber.*, **32** (1899), 321.
(3) T. Emilewicz u. St. v. Kostanecki, loc. cit., S. 696.
(4) F. Herstein u. St. v. Kostanecki, *Ber.*, **32** (1899), 318.
(5) A. Löwenbein, *Ber.*, **57** (1924), 1515.
(6) St. v. Kostanecki u. Szabránski, *Ber.*, **37** (1904), 2819.
(7) W. Feuerstein u. St. v. Kostanecki (loc. cit.) gaben den Schmp. 137–138°.

3′,4′-Methylendioxyflavon. 0.5 gr. des Flavanons wird in 5 c.c. reinem Benzol auf einem schwach siedenden Wasserbade gelöst, der Lösung 1.25 gr. Phosphorpentachlorid zugesetzt und weiter erhitzt. Bald färbt sich die Lösung rotbraun um, und es scheidet sich rotbraune Krystallmasse ab. Nach 10 Minuten werden sie scharf abgesaugt, mit wenig Benzol ausgewaschen und in 3 c.c. Alkohol eingetragen. Sie löst sich dabei mit gelinder Wärmeentwickelung. Diese alkoholische Lösung erstarrt nach einigen Sekunden zu einem gelben Krystallbrei. Dies wird sofort abfiltriert und mit wenig kaltem Alkohol gewaschen, wobei die rote schmierige Substanz in Lösung geht. Die hinterbleibende gelblich gefärbte Krystallmasse wird aus Alkohol umkrystallisiert, in welchem sie etwas schwer löslich ist. Man erhält sie ganz rein durch weitere Umkrystallisationen aus Ligroin. Sehr feine farblose Nadeln vom Schmp. 206°. ($C_{16}H_{10}O_4$. Ber.: C=72.18, H=3.76; Gef.: C=72.05, H=4.10%).

Mit conz. Schwefelsäure betupft, lösen sich die Krystalle mit gelber Farbe darin auf. Mit Eisenchlorid zeigt die Substanz keine Färbung. In sehr verdünnter alkoholischer Lösung tritt eine ziemlich intensive blaue Fluorescenz auf.

3′,4′-Methylendioxyflavonol. Auf einem kochenden Wasserbade werden einer Lösung von 3,′4′-Methylendioxyflavanon (2 gr.) in Alkohol (120 c.c.) abwechselnd conz. Salzsäure (20 gr.) und Amylnitrit (3 gr.) in kleinen Portionen zugesetzt. Beim Erkalten scheiden sich sofort gelbe Nadeln reichlich aus. Man filtriert sie ab, wäscht mit Wasser, trocknet und krystallisiert aus Alkohol um. Blassgelbe Nadeln vom Schmp. 214–215°.

Zuerst hielt ich diese Substanz für das 3′,4′-Methylendioxy-3-isonitrosoflavanon als die natürliche Folge der Reaktion. Beim Ausführen der Mikro-Dumas-Bestimmung verriet sich, aber, die Abwesenheit von Stickstoff in ihrem Molekül. Auch die Elementaranalyse ($C_{16}H_{10}O_5$. Ber.: C=68.08, H=3.54; Gef.: C=68.25, H=4.10%) und der höher liegende Schmelzpunkt weisen darauf hin, dass es hierbei das 3′,4′-Methylendioxyflavonol vorliegt, welches bei diesem Vorgange direkt entstanden ist, ohne dass das Isonitrosoflavanon als Zwischenprodukt abgefangen werden konnte.

Mit conz. Schwefelsäure betupft, färbt sie sich rotbraun; die Lösung ist auch von gleicher Farbe. Mit Eisenchlorid erzeugt sie eine bräunlich violette Färbung, ähnlich wie alle andere Flavonole. Sehr verdünnte alkoholische Lösung liefert eine grünlich blaue Fluorescenz.

3′,4′-Methylendioxyflavonolmethyläther. Das Flavonol wird in methylalkoholischer Lösung mit Diazomethan methyliert. Aus Alkohol umkrystallisiert, bildet der Methyläther weisse Prismen vom Schmp. 155°. ($C_{17}H_{12}O_5$. Ber.: 10.4%. OCH_3; Gef.: 10.5%. OCH_3).

Die Substanz zeigt keine Farbenreaktion mit Ferrichlorid: mit conz. Schwefelsäure betupft, färbt sich die Krystallmasse braunrot, wie es bei den vorigen Substanzen der Fall ist.

3′,4′-Dimethoxy-2-oxychalkon. Eine Lösung von Veratrumaldehyd (12.5 gr.) und 2-Oxyacetophenon (10 gr.) in Alkohol wird mit 50 proz. wässriger Natronlauge (25 gr. Natriumhydroxyd) versetzt und auf einem Wasserbade unter Rückfluss drei Stunden lang erhitzt. Das erhaltene gelbe krystallinische Natiumsalz des Chalkons wird mit verdünnter Salzsäure zersetzt und das nun frei gewordene Chalkon aus absolutem Alkohol umkrystallisiert. Gelbrote, sechsseitige Plättchen vom Schmp. 117°. ($C_{17}H_{16}O_4$. Ber.: C=71.8, H=5.6; Gef.: C=71.71, H=5.96%).

In alkoholischer Lösung gibt es mit Eisenchlorid eine braune Färbung. Mit conz. Schwefelsäure betupft, färben sich die Krystalle rotbraun.

3′,4′-Dimethoxy-2-acetoxychalkon. Das Chalkon wird mit siedendem Essigsäureanhydrid unter Zusatz von einigen Tropfen Pyridin leicht acetyliert. Das Produkt wird aus Alkohol mehrmals umkrystallisiert. Farblose, sechsseitige Plättchen vom Schmp. 90°. ($C_{19}H_{18}O_5$. Ber.: C=69.6, H=5.5; Gef.: C=69.3, H=5.6%).

3′,4′-Dimethoxyflavanon. 3′,4′-Dimethoxy-2-oxychalkon (3 gr.) wird auf einem siedenden Wasserbade in 150 c.c. Alkohol gelöst, der Lösung wird 10 proz. Schwefelsäure eingetropft, bis eine bleibende weisse Trübung entsteht. Dieselbe wird durch weitere Zugabe von einiger Menge Alkohol wieder in Lösung gebracht, und man fährt mit dem Erhitzen fort. Nach 20-stündigem Sieden wird die nun hellgelbe Lösung in eine offene Schale hineingegossen und stehen gelassen. Dabei scheiden sich blassgelbe glitzernde schuppenartige Krystalle aus, welche abgesaugt, mit Wasser gewaschen und in warmem Schwefelkohlenstoff gelöst werden. Nach kurzer Zeit beginnt die Ausscheidung von weissen Krystallen, welche aus Alkohol in farblosen monoklinen Tafeln auskrystallisierten. Schmp. 126°. ($C_{17}H_{16}O_4$. Ber.: C=71.8, H=5.6; Gef.: C=71.98, H=6.31%).

Die Substanz gibt keine Farbenreaktion mit Eisenchlorid; mit conz. Schwefelsäure betupft, färben sich die Krystalle rotbraun.

3′,4′-Dimethoxyflavon. Das Flavanon wird wie bei dem 3′,4′-Methylendioxyflavon in benzolischer Lösung mit Phosphorpentachlorid behandelt. Die Phosphorverbindung wird durch Eintragen in wenig kalten Alkohol zersetzt. Diese alkoholische Lösung wird in viel Wasser eingetragen, gelinde erwärmt und mit Glasstab an den Wandungen gerieben. Bald scheiden sich weisse feinwollige Nadeln aus, welche nach mehrmaligen Umkrystallisieren aus Alkohol weisse prismatische Nadeln vom Schmp. 156° geben. ($C_{17}H_{14}O_4$. Ber.: C=72.3, H=4.9; Gef.: C=72.02, H=5.11%).

Mit conz. Schwefelsäure wird die Verbindung mit rotgelber Farbe aufgenommen; mit Eisenchlorid entsteht keine Färbung in alkoholischer Lösung. Selbst eine sehr verdünnte alkoholische Lösung zeigt eine blaue Fluorescenz, wie es bei dem 3',4'-Dimethoxyflavon der Fall ist.

3',4'-Dimethoxy-3-isonitrosoflavanon. Eine siedende alkoholische Lösung von 3',4'-Dimethoxyflavanon wird mit Amylnitrit und conz. Salzsäure sukzessiv in kleinen Portionen versetzt. Nach dem Erkalten wird die Reaktionsflüssigkeit in viel Wasser eingegossen. Die zuerst weiss trübende Flüssigkeit scheidet beim Stehen übernacht gelbe amorphe Masse ab, welche trotz wiederholten Versuchen nicht zur Krystallisation gebracht werden konnte und deshalb durch Fällen mit Essigsäure aus der Lösung in verdünnter wässriger Natronlauge gereinigt wurde. Sie schmilzt unscharf bei 125–127°. ($C_{17}H_{15}O_5N$. Ber.: N = 4.4; Gef.: N = 4.7%).

3',4'-Dimethoxyflavonol. Das Isonitrosoflavanon wird wie bei dem 3',4'-Methylendioxyflavonol behandelt. Aus Alkohol umkrystallisiert, stellt das Flavonol gelbe Nadeln vom Schmp. 202° dar. ($C_{17}H_{14}O_5$. Ber.: C = 68.45, H = 4.69; Gef.: C = 68.18, H = 6.64%).

Mit conz. Schwefelsäure werden die Krystalle auch rotbraun gefärbt; mit Eisenchlorid tritt eine braunviolette Färbung auf. In sehr verdünnter alkoholischer Lösung zeigt die Substanz eine schwach grünlichgelbe Fluorescenz.

3',4'-Dimethoxyflavonolmethyläther. Das Flavonol wurde in einem Gemisch von Methylalkohol und Aceton gelöst und mit Diazomethan methyliert. Aus Alkohol umkrystallisiert, stellt der Methyläther gelblich gefärbte Warzen von feinen Nadeln dar. Schmp. 168–169°. ($C_{18}H_{16}O_5$. Ber.: 9.9%. OCH_3; Gef.: 9.7%. OCH_3).

Die Substanz zeigt keine Phenolreaktion mit Eisenchlorid.

Zum Schluss sei es mir gestattet, dem Herrn Prof. K. Shibata für seine gütige Leitung und Anregung meinen Dank auszusprechen.

März 1927.

Botanisches Institut,
Kaiserl. Universität zu Tokyo.

ON THE BASIC NITROGEN COMPOUNDS FROM FUSHUN SHALE TAR, I.[1]

By Takashi EGUCHI.

Received April 28, 1927. Published June 23, 1927.

The presence of nitrogen compounds in shale tar has long been recognized, but little is known of their chemical nature, owing to the fact that they may be present in tar in an amount rarely exceeding 1% and that the character of the bases would vary according to the conditions of the distillation of the shale, such as the type of retort used, the temperature and the time of heating.

Moreover, in the begining of the tar industry, the nitrogen constituents of shale or of coal were utilized by transforming them into ammonia, and the use of high temperature in distillation, tends to increase the yield of ammonia at the expense of the basic compounds normally found in the tars, which are for the most part relatively unstable toward heat.[2]

Since the Great War, the rapid increase in the consumption of gasoline, making heavy demands on pyridine bases as denaturants for the grain alcohol which is used as one of the constituents of some gasoline substitutes, opens the way for scientific researches into the nature of the nitrogenous substances in tars.[3]

Pyridine and its homologues have already been reported as present in Scottish and American Shale Oils; T. C. Garrett and J. A. Smythe[4] who worked on the basic constituents extracted from Scottish shale tar, have reported that pyridine, 2-methyl pyridine, 2:6-dimethyl pyridine, 2:4-dimethyl pyridine, 2:5-dimethyl pyridine, 2:3-dimethyl pyridine and 2:4:6-trimethyl pyridine were composed of the "green naphtha," with about a 0.3 per cent. yield by volume.

G. C. Robinson and his co-workers[5] have comfirmed that the bases of the isoquinoline series occurred in basic fractions boiling at 270° and 390°. The basic nitrogen compounds of American shale oil,[6] especially of the oil of the Colorado field, according to the investigations which are being carried

(1) Contribution from the Scientific Research & Experimental Branch, Imperial Naval Fuel Depot, No. 1.

(2) P. E. Spielmann, "The Constituents of Coal Tar," (1924), 157; R. H. Mckee, "Shale Oil" (1925), 116.

(3) E. H. Leslie, "Motor Fuels," (1923), 13 & 482.

(4) *J. Chem. Soc.*, **81** (1902), 449; **83** (1903), 763.

(5) R. H. Mckee, "Shale Oil," (1925), 175.

(6) Ibid., p. 120.

out in the Chemical Engineering Laboratories of Columbia University, seem to be composed mostly of pyridine and its homologues, but not of the quinoline or the isoquinoline bases. It is remarkable, though the significance of the basic compounds in the natural product is not immediately apparent, that the majority of the nitrogen compounds in the shale oil are nitrogen-ring compounds, but not substitution products of the aromatic series as we noticed of the nitrogen bases occur in petroleum.(1)

The low temperature tar of Fushun coal, according to Y. Oshima and K. Ishibashi,(2) contains 0.67% of basic substances and among these substances 2-methyl pyridine, 3:4-dimethyl pyridine and 2:4:6-trimethyl pyridine were confirmed to occur, and the presence of aniline and its homologues were also confirmed. To our interest, the crude tar of Fushun shale has the highest nitrogen base content of any known, viz., 2–4%. It stands in nitrogen content near to Californian petroleum, which is 2.39%.(3)

The isolation in a pure state of the nitrogenous substances from the Fushun shale oil, and the study of the chemical and physical properties of the purified substances, aroused the writer's interest, in relation to some evidences for the significance of the presence of nitrogenous compounds in tar, which might give some suggestion for the consideration of the mechanism of the chemical processes in the distillation of the shale, and the present investigation was undertaken.

The crude tar used for the experiment was obtained by the distillation of Fushun shales of the composition (A & B) in the vertical retort, the Oakbank Retort, in Scotland, which shows the following properties:(4)

	A.	B.
Water	3.04%	2.67%
Volatile matter.	21.05%	15.89%
Fixed carbon.	4.47%	1.34%
Ash.	71.44%	80.10%

Tar. C=83.80; H=11.53; N=0.45; O=3.63; S=0.59; d_4^{15}=0.864.

	Fractions.	Yield (Vol.)
1.	— 200°	3%
2.	200° – 250°	25%
3.	250° – 300°	27%
4.	300° – 350°	23%
5.	above 350°	22%

600 litres of the crude tar were fractionated under atmospheric pressure

(1) Engler-Höfer, "Das Erdöl," I. (1913), 479.
(2) *J. Soc. Chem. Ind. Japan*, **29** (1925), 445.
(3) C. F. Mabery & L. G. Wesson, *J. Am. Chem. Soc.*, **42** (1920), 1014.
(4) Refer: T. Kimura, *Reports of Invest. (Japanese) Central Lab., South Manchuria Railway Co. Ltd.*, **10** (1925), 507.

TABLE 1.

Fraction.	Distillate in gr.	$\frac{dw}{dT}$	d_4^{25}	n_D^{25}	Mol. wt.
128°–130°	32.5	16.3	0.9420	1.4970	95.4
130–132	8.8	4.4	0.9441	1.4970	
132–134	4.0	2.0	0.9476	1.4963	
134–136	1.5	0.8			
136–138	2.0	1.0	0.9376	1.4965	
138–140	2.0	1.0			
140–142	5.0	2.5	0.9328	1.4977	
142–143	17.7	17.7	0.9322	1.4979	
143–144	70.0	70.0	0.9320	1.4980	103.3
144–145	44.5	44.5	0.9330	1.4979	
145–146	15.0	15.0	0.9363	1.4973	
146–148	20.0	10.0	0.9312	1.4979	
148–150	11.5	5.8	0.9367	1.4958	
150–153	12.5	4.1	0.9312	1.4962	
153–156	15.3	5.1	0.9305	1.4964	
156–157	9.5	9.5	0.9265	1.4972	
157–158	39.3	39.3	0.9271	1.4969	
158–159	104.4	104.4	0.9260	1.4977	110.0
159–160	74.0	74.0	0.9265	1.4977	
160–161	14.	14	0.9312	1.4979	
161–163	26	13	0.9269	1.4979	
163–165	26	13	0.9272	1.4975	
165–167	18	9	0.9235	1.4975	
167–169	36	18	0.9214	1.4974	
169–170	29	29	0.9201	1.4973	
170–171	70	70	0.9180	1.4976	120.0
171–172	73	73	0.9185	1.4981	120.1
172–173	37	37	0.7202	1.4985	121.7
173–174	32	32	0.9213	1.4990	121.4
174–175	24	24	0.9240	1.4990	121.6
175–176	29	29	0.9242	1.4989	121.4
176–177	24	24	0.9271	1.4988	121.7
177–178	28	28	0.9268	1.4986	121.5
178–179	34	34	0.9241	1.4986	123.0
179–180	23	23	0.9237	1.4977	125.3
180–182	23	12	0.9186	1.4976	127.4
182–184	22	11	0.9194	1.4975	131.1
184–186	45	23	0.9145	1.4977	132.1
186–187	30	30	0.9133	1.4182	131.9
187–188	52	52	0.9173	1.4985	133.3
188–189	29	29	0.9178	1.4991	131.7
189–190	41	41	0.9191	1.4994	132.1
190–191	29	29	0.9188	1.4996	131.9
191–192	26	26	0.9212	1.5000	131.8
192–193	15	15	0.9249	1.5001	133.4
193–194	16	16	0.9258	1.5001	133.9
194–196	24	12	0.9251	1.5001	133.9
196–198	20	10	0.9285	1.5022	137.2
198–200	14	7	0.9313	1.5032	137.2
200–202	61	31	0.9261	1.5042	141.5
202–204	49	25	0.9268	1.5041	141.6
204–206	32	16	0.9257	1.5043	140.9
206–208	25	13		1.5050	142.1
208–210	16	8		1.5060	
210–214	24	6		1.5065	
214–218	29	7		1.5086	

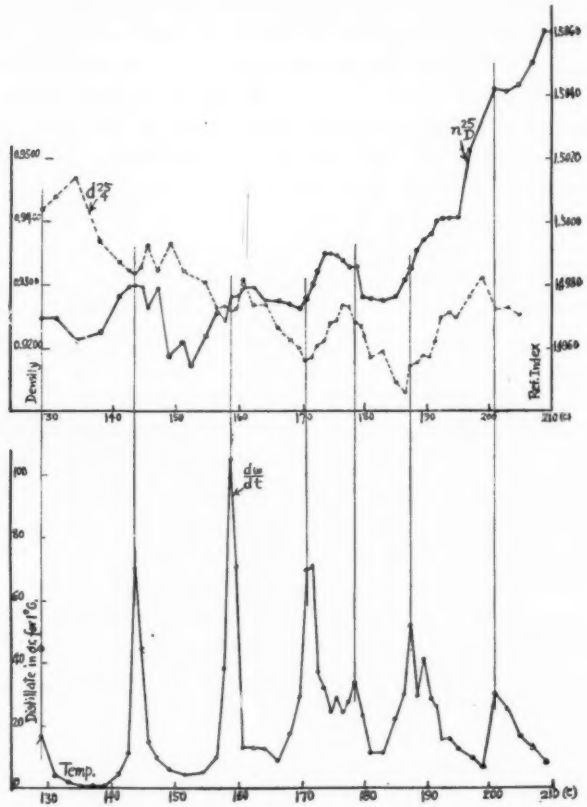


Fig. 1.

and thereby 106 litres of the fraction b. p. 220°–250° were obtained which were used in this experiment, and treated with 30% sulphuric acid to extract the basic substance; the crude base recovered amounted to 3550 c.c., (corresponding to about 0.6% by volume of the crude tar used), and they were distilled out between 100°–280°, and the specific gravity was about 0.979 at 15°. The nitrogen bases occurring in the fraction faintly show pyrrol reactions, but negatively the carbylamine reaction for primary amines and the Liebermann nitroso reaction for secondary amines. The presence of the tertiary bases of the pyridine series is shown in the behavior toward picric acid, ferrocyanic acid and mercuric chloride.

For the isolation of individual bases in an approximately pure state, 1965 gr. of the basic fraction boiling to 220°, was subjected to fractional dis-

tillation; it was fractionated carefully three times in a flask with a Norton & Otten's Six-column dephlegmator of 45 cm. length, and then seven successive fractional distillations through Hempel's glass dephlegmator of 120 cm. length, 2 cm. diameter, which contains 600 glass beads of 4 mm. diameter, the operation was continued at the rate of one or two drops of distillate every two seconds, and the results of the 10th distillation, the weight of each distillate, the ratio of weight and temperature range dw/dt, specific gravity, and index of refraction are shown in Table 1. The temperature-weight curve of the results shown in Fig. 1 shows the seven maxima which indicate the presence of some definite compounds in the regions.

1. 2-Methyl Pyridine.[1] 2-Methyl pyridine which was assumed to be composed of the fraction, b. p. 128°–130°; $d_4^{25}=0{,}9420$; $n_D^{25}=1.4970$, 30 gr. of the fraction dissolved in dilute hydrochloric acid were added to 181 gr. of mercuric chloride dissolved in 2000 c.c. of water, and on standing the solution for a while at 20°C., 215 gr. of prismatic crystals of the double salt of mercury chloride were deposited. On purifying by recrystallisation twice from a dilute acidic solution, the pure double salt of melting-point 153°–154°, was isolated, the yield was 180 gr. On analysis, Hg was found to be 69.06%, while theory requires 69.67% for $C_6H_7N{\cdot}HCl{\cdot}2HgCl_2$.

To liberate the free base, 60 gr. of sodium hydroxide were added to 180 gr. of the purified salt dissolved in 2000 c.c. of water, the free base extracted with benzene, distilled off the solvent, after fixed with hydrochloric acid, decomposed with caustic soda, dried with fused caustic potash and then distilled. It distilled completely at 129°.20–129°25 under 758.5 mm. and show the following physical constants:

d_4^{25}(in vacuo)$=0.9400$; $n_D^{25}=1.4983$; $n_C^{25}=1.4939$; $n_F^{25}=1{:}5097$; $n_{G'}^{25}=1.5197$.

0.1320 Gr. of the subst. gave 0.3745 gr. CO_2 and 0.0895 gr. H_2O. 0.2500 Gr. subst. gave 33.0 c.c. N_2 at 25° and 671 mm. (Found: C=77.42; H=7.59; N=15.15; Mol. wt., 93.8. C_6H_7N requires C=77.36; H=7.58; N=15.05 %; Mol. wt., 93.1).

It was identified as 2-methyl pyridine by the oxidation of 3 gr. of the purified base with a 2% aqueous solution of 10.4 gr. potassium permanganate, the pyridine-2-carboxylic acid, thus obtained, was purified by converting it into the copper salt with a copper acetate solution. The copper salt, showing the characteristic appearance of the bluish-violet platy crystals of the salt of pyridine-2-carboxylic acid, was analysed for confirmation with the following results:

0.113 Gr. of the salt gave 0.0115 gr. loss on heating, 0.1694 gr. CO_2, 0.0252 gr. H_2O and 0.0258 gr. CuO. (Found: C=41.53; H=2.53; Cu=18.52;

(1) P. E. Spielmann, "The Const. Coal Tar," (1924), 183.

$H_2O = 10.33$. $(C_5H_4N \cdot CO_2)_2Cu \cdot 2H_2O$ requires C = 41.90; H = 2.35; Cu = 18.50; $H_2O = 10.48\%$).

The free acid isolated from the copper salt shows a reddish yellow colour reaction with ferrous sulphate.

2. 2:6-Dimethyl Pyridine.[1] The fractions (1) b. p. 143°–144°; $d_4^{25} = 0.9320$; $n_D^{25} = 1.4980$; (2) b. p. 144°–145°; $d_4^{25} = 0.9330$; $n_D^{25} = 1.4979$ were regarded as a mixture of mono- and dimethyl pyridine from their physical constants and the molecular weight determination (mean Mol. wt. 103), and 40 gr. of the former fraction and 50 gr. of the latter were combined together, dissolved in a dilute hydrochloric acid solution, to which 250 gr. of mercuric chloride in total were added in several doses and 185 gr. of platy crystals of the double salt were obtained. Purifying twice from the dilute acidic solution, 171 gr. of pure salt of a melting point 191°–191°.5 were obtained, which on analysis, agrees in compostion with the formula $C_7H_9N \cdot HCl \cdot HgCl_2 \cdot H_2O$. (Hg = 46.85; Cl = 24.61%). 170 gr. of the pure salt were decomposed with a concentrated sodium hydroxide solution, and the free base was dried over fused caustic potash and distilled. 39.5 gr. of the pure base, thus obtained, were distilled out completely at 143°.85–143°.87 under 757.4 mm.

It was a non-disagreeable odours oil, completely miscible with water at 25°, and showed the following constants:

d_4^{25} (in vacuo) = 0.9183; $n_D^{25} = 1.4953$; $n_C^{25} = 1.4910$; $n_F^{25} = 1.5065$; $n_{G'}^{25} = 1.5164$.

0.0967 Gr. subst. gave 0.0738 gr. H_2O and 0.2780 gr. CO_2. 0.2951 Gr. subst. gave 38.8 c.c. N_2 at 29° and 759 mm. (Found: C = 78.41; H = 8.54; N = 13.32; Mol. wt., 106.5. C_7H_9N requires C = 78.45; H = 4.47; N = 13.08%; Mol. wt., 107.1)

5 Gr. of the base were oxidized with 35 gr. of potassium permanganate in dilute solution, and dipicolinic acid formed by the oxidation, was obtained, and this was recrystallized from the aqueous solution. The yield was 5.3 gr. It melts at 238°.5, whereas Conrad & Epstein[2], and Collie[3] have recorded its melting point as 237° and 236°, respectively. The acid recrystallized from boiling alcohol, was found to melt at 226°.5–227°, as stated by A. Ladenburg & C. F. Roth[4] (226°) and also by C. Paal and C. Demeler[5], (226°–227°) for the melting point of the same acid.

On analysis of the acid with m. p. 226°, the results obtained were:

0.1008 Gr. subst. gave 0.1858 gr. CO_2 and 0.0278 gr. H_2O. (Found: C = 50.27; H = 3.09. $C_5H_3N(CO_2H)_2$ requires C = 50.28; H = 3.02%)

(1) P. E. Spielmann, loc. cit., P. 187.
(2) *Ber.*, **20** (1887), 162.
(3) *J. Chem. Soc.*, **59** (1891), 177.
(4) *Ber.* **18** (1885), 52.
(5) Ibid., **30** (1897), 1502.

3. **2:4-Dimethyl Pyridine.**[1] Both of the two fractions (1) b. p. 158°–159°; $d_4^{25}=0.9260$; $n_D^{25}=1.4977$, (2) b. p. 159°–160°, $d_4^{25}=0.9265$; $n_D^{25}=1.4977$, seem to be a mixture of lutidines and collidines as indicated by the mean molecular weight 110. To isolate the lutidine-2:4-dimethyl pyridine, in a pure state, the mixed oil derived from 55 gr. of the first fraction, and 55 gr. of the second, dissolved in a dilute hydrochloric acid solution, was added to the solution of 544 gr. of mercuric chloride dissolved in 8 litres of hot water. Long needle crystals (m. p. 124°) of glasswool-like lustre were deposited, recrystallized twice from hot water, and 240 gr. of the pure double salt of mercuric chloride with a melting-point of 131°–132° were obtained. It gave Hg=57.17, on analysis, which corresponds to Hg=56.94 for $C_7H_9N\cdot HCl\cdot 2HgCl_2\cdot H_2O$. 210 gr. of the salt were decomposed with 600 c.c. of a 10% caustic soda solution, and 30.5 gr. of a colourless base were separated, and this was dried with fused caustic potash and distilled.

It distilles completely at 157°.83–157°.85 under 758 mm., and dissolves in an equal quantity of water at 35° and shows these constants:

d_4^{25} (in vacuo)=0.9271; $n_D^{25}=1.4984$; $n_C^{25}=1.4942$; $n_F^{25}=1.5095$; $n_{G'}^{25}=1.5190$.

0.1184 Gr. subst. gave 0.3392 gr. CO_2 and 0.0915 gr. H_2O. 0.3319 Gr. subst. gave 40.2 c.c. N_2 at 33° and 760 mm. (Found: C=78.13; H=8.65; N=13.27; Mol. wt., 106.5. C_7H_9N requires C=78.45; H=8.47; N=13.08%; Mol. wt., 107.1)

The base was identified as 2:4-dimethyl pyridine by oxidation, 4 gr. of the base with an aqueous solution of 28 gr. potassium permanganate, and the dicarboxylic acid obtained by the oxidation was converted into the copper salt with copper acetate, which was separated into two crops by their solubility in water, the one being cobalt-coloured crystals which are insoluble in water, and the other bluish green crystals, more soluble in water than the former, and the yield is 2.3 gr. and 3.1 gr., respectively.

On analysis 0.1024 gr. of the former salt gave 0.1496 gr. CO_2, 0.0264 gr. H_2O and 0.0192 gr. CuO. (Found: C=39.84; H=2.89; Cu=15.21. $(C_5H_3N\cdot CO_2H\ CO_2)_2Cu.H_2O$ requires C=40.61; H=2.44; Cu=15.37%)

The free acid recovered from the copper salt by means of hydrogen sulphide gas, shows the melting point (244°) of 2:4 lutidinic acid.

The second copper salt also gave 2:4 lutidinic acid with a m. p. of 247° and the analytical results of the free acid and its copper salt, agree well with those of the acid mentioned in the literature.

0.1665 Gr. subst. gave 0.0131 gr. loss on heating at 96° for 4 hours, and 0.0533 gr. CuO. (Found: Cu=27.76. $C_5H_3N.(CO_2)_2.Cu.H_2O$ requires Cu=27.81 %).

(1) P. E. Spielmann, loc. cit., p. 186.

0.1002 Gr. free acid gave 0.0103 gr. loss on heating at 110° for 3 hours. 0.0873 Gr. dried acid gave 0.1623 gr. CO_2 and 0.0250 gr. H_2O. (Found: C=50.70; H=3.28. $C_5H_3N.(CO_2H)_2.H_2O$ requires 10.28 % of the water of crystallization).

4. 2:6-Methyl Ethyl Pyridine. The mother liquor separated from the crystals of the double salt of mercuric chloride of 2:4 dimethyl pyridine hydrochloride, remains on concentration a colourless oily salt which liberates a base of disagreeable odour, even when the salt is diluted with water. The free base which is composed mostly of methyl ethyl pyridine with some dimethyl pyridine, was treated in a benzene solution with picric acid to remove the latter base completely from the former by converting it into picrate which is slightly soluble in solvents and methyl ethyl pyridine was isolated in a free state from the amorphous picrate which remained in the mother liquor separated from dimethyl pyridine picrate in an benzene solution. The yield is 10 gr. and in consequence of the small quantity of the substance no accurate reading of the boiling point was possible; it distiles at 160°–161° und 760 mm., dissolves in 55 times of water at 30°, and shows the following constants: $d_4^{25}=0.9207$; $n_D^{25}=1.4950$; $n_C^{25}=1.4908$; $n_F^{25}=1.5057$; $n_{G'}^{25}=1.5151$.

0.1073 Gr. subst. gave 0.3114 gr. CO_2 and 0.0881 gr. H_2O. 0.3537 Gr. subst. gave 36.2 c.c. N_2 at 29° and 759 mm. (Found: C=78.93; H=9.19; N=11.56; Mol. wt., 118. $C_8H_{11}N$ requires C=79.27; H=9.16; N=11.57%; Mol. wt., 121.1)

The base was confirmed as 2:6-methyl ethyl pyridine, by oxidation of 2.5 gr. of the base with 27 gr. potassium permanganate, the free dicarboxylic acid purified from the copper salt isolated from the oxidation product was found to melt at 227°.

5. 2:4:6: Trimethyl Pyridine. For isolation of this base in a pure state, two fractions, 50 gr. of one fraction with a b.p. of 170°–171°; $d_4^{25}=0.9180$; $n_D^{25}=1.4976$; Mol. wt. 120, and 50 gr. of the other with a b.p. of 171°–172°; $d_4^{25}=0.9185$; $n_D^{25}=1.4981$: Mol. wt. 120, combined together and treated with a mercuric chloride solution, and collected a crop of platy crystals with a m.p. of 156° deposited on each addition of the mercuric chloride. The yield was 240 gr. On purifying, 205 gr. of the crystals melting at 157°–157°.5 were obtained, and these gave Hg=56.71 ($C_8H_{11}N.HCl.2HgCl_2.1/2H_2O$ requires Hg=56.54 %).

The free base isolated in pure state from 200 gr. of the purified salt as usual amounted to 32.5 gr. It distils completely at 170.47°–170.51° under 762.3 mm. and has a nondisagreeable characteristic odour. It dissolves in 30 times of water at 20° and shows the following constants:

d_4^{25}(in vacuo)=0.9101 ; n_D^{25}=1.4959; n_C^{25}=1.4919; n_F^{25}=1.5069 ; $n_{G'}^{25}$=1.5164.

0.1055 Gr. subst. gave 0.3061 gr. CO_2 and 0.0862 gr. H_2O. 0.3150 Gr. subst. gave 32.0 c.c. N_2 at 25° and 767 mm. (Found : C=79.13 ; H=9.15 ; N=11.75, Mol. wt., 121.8. $C_8H_{11}N$ requires C=79.27; H=9.16; N=11.57%; Mol. wt., 121.1).

For identification of the base to be 2:4:6-trimethyl pyridine, 5 gr. of the purified base were oxidized with an aqueous solution of 53 gr. of potssium permanganate, and pyridine-2:4:6 tricarboxylic acid resulted by oxidation of the base purified from its silver salt, was found to melt at 227°.5. The yield was 5.3 gr.

0.1000 Gr. subst. gave 0.1441 gr. CO_2 and 0.0341 gr. H_2O. (Found : C=39.30 ; H=3.82. $C_5H_2N(CO_2H)_3.2H_2O$ requires C=38.85 ; H=3.61%).

The nitrogeous substances were isolated by extraction from the fraction b.p. 220°–250°, of Fushun shale oil by dilute sulphuric acid, liberation with alkali, drying and fractionation. Fach fraction is treated in its dilute hydrochloric acid solution with mercuric chloride, from which the bases were separated as a double salt of mercuric chloride, purified from the dilute acid solution, and finally they were again liberated in a free state by alkali, and distilled. 2-Methyl pyridine, 2:6-dimethyl pyridine, 2:4-dimethyl pyridine, 2:6-methyl ethyl pyridine and 2:4:6-trimethyl pyridine were proved to occur in the tar and identified by oxidation with a potassium permanganate solution, transforming them to the corresponding carboxylic acids.

The writer's samples which were isolated from the shale tar were in a highly purified state and no work of preparation of auch highly purified bases of the pyridine series has been described except that of J. G. Heap, W.I. Jones and J.B. Speakman.(1) They prepared the bases of the pyridine series from tar by fractionation and purification through the zinc chloride compounds.

In the following table, the physical constants of the writer's samples are shown with those of the bases of the pyridine series obtained by other chemists.(2)

(1) *J. Am. Chem. Soc.*, **43** (1921), 1926.

(2) K. V. Auwers & R. Kraul, *Z. physik. Chem.*, **116** (1925), 448; Landolt-Börnstein-Roth, "Tabellen."; "International Critical Tables." I.; T. C. Garrett and J. A. Smythe Loc. cit.

TABLE 2.

	Pyridine	2-Methyl Pyridine	2-6-Dimethyl Pyridine	2-4-Dimethyl Pyridine	2-6-Methyl-ethyl Pyridine	2-4-6-Trim-ethyl Pyridine
b. p.	(1) 115°–6°	129°.5 (763 mm.)	142°.5	159°–.5°	—	170°.5 (763 mm.)
	(2) 115°.3 (760 mm.)	128°–9° (760 mm.)	137°.5 (about)	157°.1 (760 mm.)	—	—
	(3) 115°.3 (760 mm.)	129°.3 (759 mm.)	143°.9 (758 mm.)	157°.9 (758 mm.)	160°–1°	170°.5 (762 mm.)
d_4^{25}	(2) 0.9776	0.9404	0.9200	0.9273	—	—
	(3) —	0.9400	0.9183	0.9271	0.9207	0.9101
n_C^{25}	—	1.4939	1.4910	1.4942	1.4908	1.4919
n_D^{25}	—	1.4983	1.4953	1.4984	1.4950	1.4959
n_F^{25}	—	1.5097	1.5065	1.5095	1.5057	1.5069
$n_{G'}^{25}$	—	1.5197	1.5164	1.5190	1.5151	1.5164
Mα	23.89 (A)	28.82	33.77	33.64	38.08	38.60
MD	24.04 (A)	29.04	34.02	33.88	38.36	38.86
Mβ	24.55 (A)	29.60	34.67	34.52	39.06	39.59
Mγ	24.96 (A)	30.09	35.24	35.06	39.67	40.22
Mγ-Mα	1.07 (B)	1.27	1.47	1.42	1.59	1.62
Mβ-Mα	0.66 (B)	0.78	0.90	0.88	0.98	0.99
(C)	-1.44	-0.82	-0.51	-0.58	-0.42	-0.25
„	—	-0.90	-0.43	-0.56	-0.60	-0.18

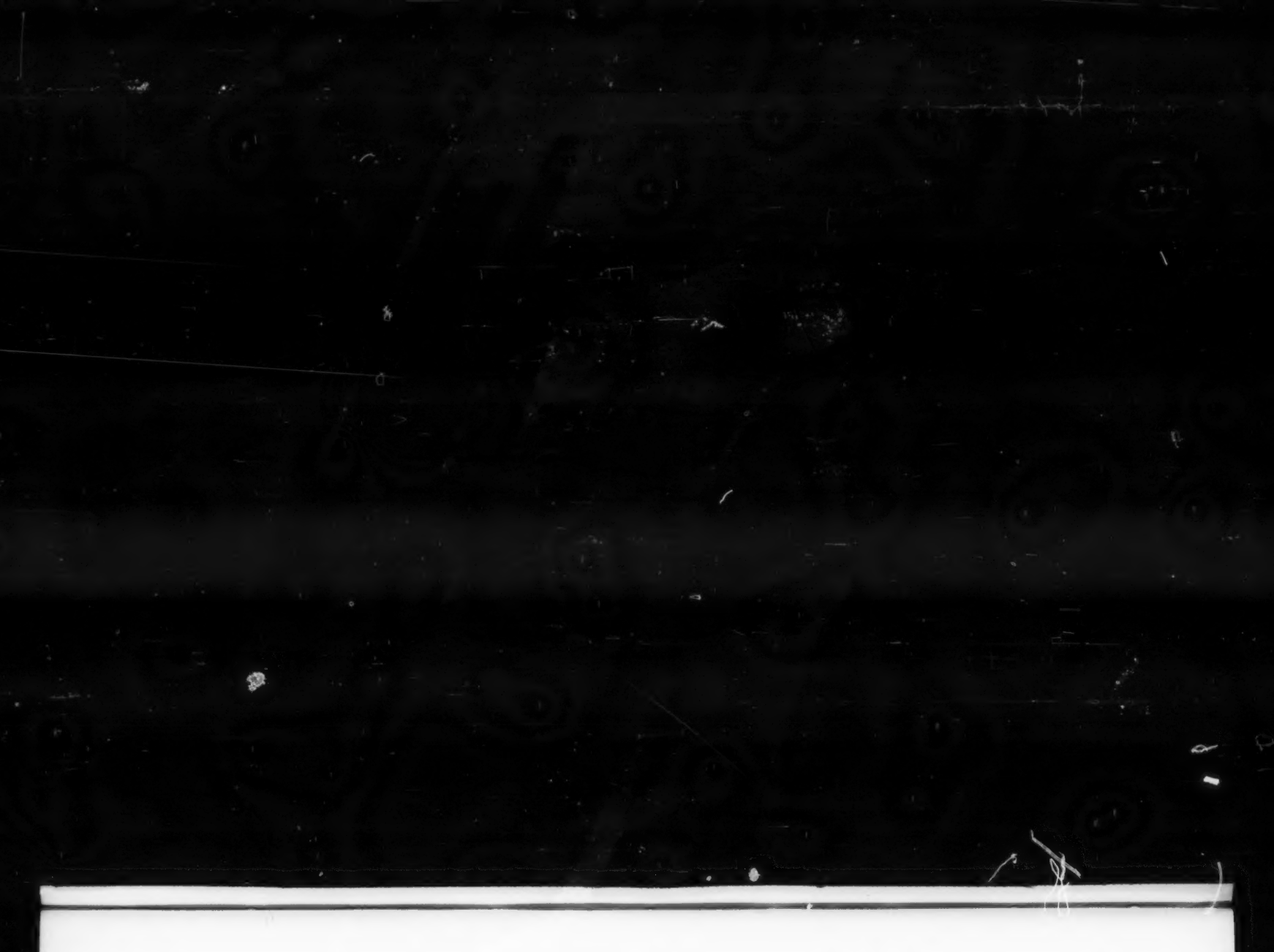
(1) F. C. Garrett and J. A. Smythe, loc. cit.
(2) J. G. Heap, W. I. Jones and J. B. Spielman, loc. cit.
(3) Writer.
(A) & (B) Landolt, Börnstein-Roth: Tabellen.
(C) K. V. Auwers & R. Kraul; *Z. Physik. Chem.*, **116** (1925), 448.

As will be seen in the forgoing table, the molecular refractive power and the dispersive power of the bases for the α, β and γ hydrogen lines and also the sodium D line have been determined, since Brühl[1] has already shown that these physical constants offer and excellent means of determining the structure of organic compounds, especially as dispersive power is more readily influenced by constitution than refractivity.

The average value for the refractive effect of the hydrogen lines α, β, γ and the sodium D line of the CH_2 group which combined with the α or γ position of the pyridine nucleus, has been calculated,[2] and the increment for the α position compared with the γ position varies about 0.13 to 0.18.

(1) *Z. physik. Chem.*, **7** (1891), 140; **16** (1895), 201; **79** (1912), 481.
(2) Refer: K. V. Auwers and R. Kraul, Ibid., **116** (1925), 448; *Ber.*, **57** (1924), 457.

There is no doubt that the effect of CH_2 depends to a certain extent on the position by which it combines with the carbonatom of the pyridine nucleus of the compounds, and it was able more exactly to elucidate the constitutive nature of the properties in the molecular dispersive power than in the molecular refractive power.

In conclusion, the writer wishes to express his gratitude to Vice-Admiral G. Yamashita, Director of the Imperial Naval Fuel Depot, Rear-Admiral T. Kishida, Chief of the Oil Department and Engineer Captain Viscount M. Kawase, Chief of the Scientific Research & Experimental Branch for their Kindness in enabling him to take part in this research, and also to Professor S. Komatsu of the Kyoto Imperial University, whose advice and encouragement have been invaluable.

The Scientific Research and Experimental Branch,
The Imperial Naval Fuel Depot, Tokuyama.